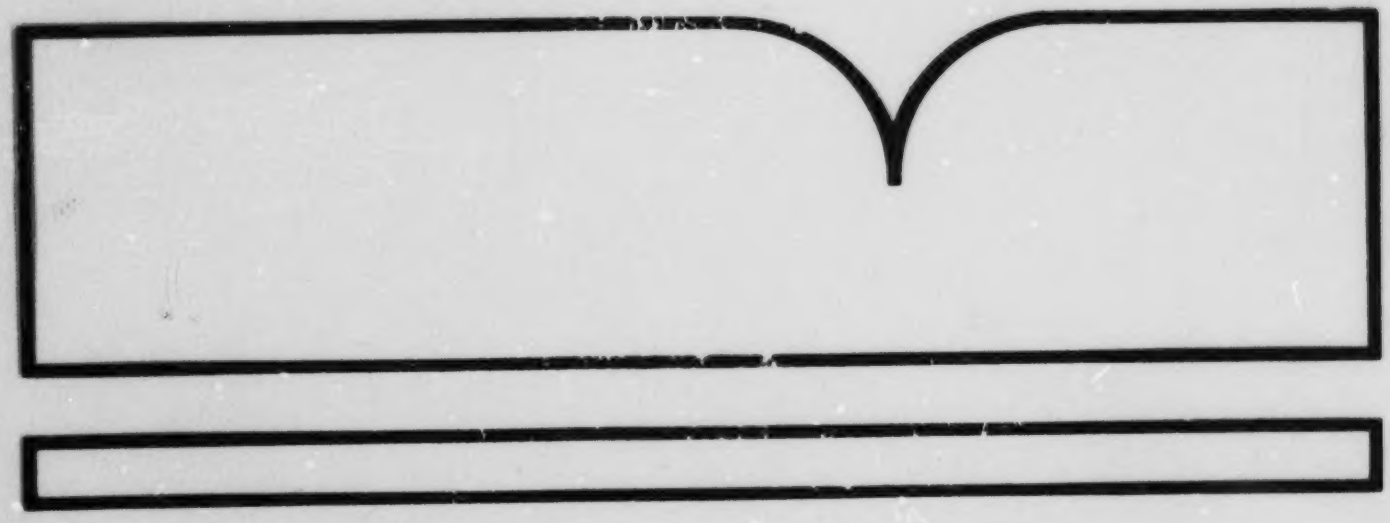
PB84-195379

Chemical and Biological Studies Related to the Water Quality of St. Louis Bay of Lake Superior

(U.S.) Environmental Research Lab.-Duluth, MN

May 84



U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-195379

EPA-600/3-84-064
May 1984

Chemical and Biological Studies Related to the Water Quality of St. Louis Bay of Lake Superior

by

A. R. Carlson and N. A. Thomas

A cooperative effort among the U.S. EPA Environmental Research Laboratory-Duluth, University of Wisconsin-Superior and University of Minnesota-Duluth

U.S. Environmental Protection Agency
Environmental Research Laboratory-Duluth
6201 Congdon Boulevard
Duluth, Minnesota 55804

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA *(Please read Instructions on the reverse before completing)*		
1. REPORT NO. EPA-600/3-84-064	2.	3. RECIPIENT'S ACCESSION NO. PB84 195379
4. TITLE AND SUBTITLE Chemical and Biological Studies Related to the Water Quality of St. Louis Bay of Lake Superior		5. REPORT DATE May 1984 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) A.R. Carlson and N.A. Thomas		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Duluth, Minnesota 55804		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Same as above		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA-600/03
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

This was a cooperative effort among the University of Wisconsin-Superior, University of Minnesota-Duluth, and U.S. EPA Environmental Research Laboratory-Duluth to develop and evaluate effluent toxicity screening methods and test methods and protocols for deriving site-specific water quality criteria. The principal components of the study were to include: (1) a chemical characterization of the main discharges to the St. Louis River and Harbor, (2) persistence of toxic pollutants in the St. Louis River and Harbor, (3) a description of the exposure times for various components of the ecosystem, (4) bioassays with St. Louis River water and resident species, (5) an assessment as to the degradation of the biologic community of St. Louis Harbor, and (6) a modeling framework to address items 1 through 5.

Because persistent toxic pollutant concentrations were not found in the WLSSD effluent and no persistent open water pollutant problems were apparent, this study was ended. The Project Report contains a series of reports on work completed.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified 20. SECURITY CLASS *(This page)* Unclassified	21. NO. OF PAGES 126 22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement oi recommendation for use.

CONTENTS

Executive Summary

A Summary of Results and Conclusions

Introduction

Water Chemistry in St. Louis Bay -- R. B. Cook and J. Ameel

St. Louis Bay Benthos Survey -- T. Roush

Seasonal Primary Production and Plankton Dynamics in St. Louis River and Harbor -- J. R. Hargis

Site-Specific Acute and Chronic Aquatic Toxicity Testing - Western Lake Superior Sanitary District Treatment Plant Effluent Studies -- D. J. Call, L. T. Brook, C. Northcott, and D. E. Hammermeister

Locomotor and Ventilatory Response of Fish Exposed to Final Treated WLSSD Effluent (A Summary) -- R. A. Drummond

Characterization of the Organic Nature of the Western Lake Superior Sanitary District Effluent - Summer 1982 (A Summary) -- R. Caple

EXECUTIVE SUMMARY

This was a cooperative effort among the University of Wisconsin-Superior, University of Minnesota-Duluth, and U.S. EPA Environmental Research Laboratory-Duluth to develop and evaluate effluent toxicity screening methods and test methods and protocols for deriving site-specific water quality criteria. The principal components of the study were to include: (1) a chemical characterization of the main discharges to the St. Louis River and Harbor, (2) persistence of toxic pollutants in the St. Louis River and Harbor, (3) a description of the exposure times for various components of the ecosystem, (4) bioassays with St. Louis River water and resident species, (5) an assessment as to the degradation of the biologic community of St. Louis Harbor, and (6) a modeling framework to address items 1 through 5.

Because persistent toxic pollutant concentrations were not found in the WLSSD effluent and no persistent open water pollutant problems were apparent, this study was ended. Following are a series of reports on work completed.

A Summary of Results and Conclusions

ST. LOUIS BAY

Water Chemistry Surveys

At the six sites, in the small embayment near the Western Lake Superior Sanitary District (WLSSD) wastewater treatment plant, ammonia, alkalinity, total phosphorus, and chloride were higher than in the control embayments.

The fraction of WLSSD effluent, estimated from chloride concentration, was 0.20-0.25 in the three sites closest to the discharge pipe and 0.05-0.10 in the three sites farthest from the discharge pipe.

Ammonia and total phosphorus appear to have a substantial sediment source in the small embayment near WLSSD.

Nutrient input budgets for St. Louis Bay revealed that 90% of the alkalinity, ammonia, and total phosphorus loadings were derived from the St. Louis River with the remainder originating from WLSSD. However, high chloride concentrations in the WLSSD effluent contribute 43% of the Cl^- loading to St. Louis Bay, compared to 57% from the St. Louis River.

Comparison of the total phosphorus input budget for 1982 with a similar budget for 1972 revealed that the WLSSD sewage treatment plant released one-fifth the total phosphorus that was released by the nine sewage treatment plants operating in 1972.

Phenol concentrations decreased from 8 to 9 $\mu g\ L^{-1}$ in the mid-1970s to 3 $\mu g\ L^{-1}$ in 1982.

The mean total phosphorus at site L (downstream from the present WLSSD plant) decreased from 110 $\mu g\ L^{-1}$ between 1972 to 1979 to 75 $\mu g\ L^{-1}$ for 1979 to 1982.

The mean ammonia concentration at site L decreased from 0.259 $mg\ L^{-1}$ (pre-1979) to 0.116 $mg\ L^{-1}$ after 1979.

Benthic Invertebrate Surveys

The benthic invertebrate surveys demonstrated noticeable differences between the WLSSD discharge bay and two bays (controls) upstream. The discharge bay contained fewer types of organisms and these are considered more tolerant of domestic effluents. The differences between the bays were less noticeable in October than in June or August.

Phytoplankton and Zooplankton Surveys

The Duluth-Superior Harbor is a complex system for pelagic sampling. Not only is the bathymetry complex, with the extensive shallows plus the deep, dredged ship channels, but the interactive flows of the St. Louis River and seiche currents from Lake Superior make point samples a function of many variables. In the shallows, particularly, the range of seasonal change can be extreme. Within this context, examination of the plankton data from Summer 1982 shows no adverse influence of the effluent from the WLSSD plant.

WLSSD EFFLUENT TOXICITY AND CHARACTERIZATION

Effluent Toxicity

The effluent was intermittently acutely toxic to aquatic organisms (fish and invertebrates) in toxicity tests. Behavioral monitoring of fish continuously exposed to the plant effluent was used to identify periods of effluent toxicity.

Increases in fish locomotor and respiratory activity correlate with fish mortality in bioassays of grab samples. Some possible causes of observed toxicity were thought to be related to elevated total residual chlorine or carbon dioxide concentrations resulting from changes in wastewater treatment in response to changes in influent conditions.

It is recommended that any future bioassays of WLSSD effluent, or the effluent from other treatment plants, be complemented with chemical analyses of total chlorine, pH (immediate and after extended aeration), carbon dioxide, alkalinity, and hardness. If possible, these tests should be coupled with sensitive aquatic organism behavioral monitoring to identify episodic periods of toxicity.

Effluent Characterization

A comparative qualitative analyses was made of the WLSSD effluent and influent, and a similar analysis was made of the effluent from the largest single contributor of industrial type organics (a pulp and paper industry) to the WLSSD influent. The isolation and concentrations in composite samples were done in threes to reflect the "acidic", "neutral", and "basic" functionalities in the components analyzed using mass spectroscopy. The mass of data is presently being incorporated into a three x three matrix (3 analyses and 3 sample sites) based on functionality. When completed an interpretation of the meaning and significance of the data will be made.

Because chlorophenols originating from WLSSD had been previously traced within the bay and into Lake Superior, a gas chromatography with electron capture detection procedure aimed at sensitivity, and a second procedure with liquid chromatography with a variable wavelength that would aid the identification of chlorophenols in complex mixtures were developed.

A detailed report containing the methods used in effluent characterization and raw data, and chlorophenol analysis procedures are available on request.

Bibliography

"An Annotated Bibliography of Environmental Research Conducted Within the St. Louis River Estuary 1903-1982" authored by Phil Devore was completed

and is only available from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161 [Order No. PB83-261-693 (EPA-600/S3-83-092)] at a cost of $10.00. This report is intended as a tool for people to locate specific types of studies conducted within St. Louis Bay and was an attempt to compile and review all of the physical, biological, and chemical studies related to the bay.

CONCLUSIONS

1. The water quality of the St. Louis Harbor has improved. Much of the improvement can be attributed to the onset of the operation of the present WLSSD wastewater treatment plant.
2. There was only a slight impact on the benthic invertebrate community from the WLSSD outfall.
3. Survey data indicates that phytoplankton and zooplankton were not demonstratably impacted by the WLSSD effluent.
4. The WLSSD plant is currently treating its waste to a higher degree than the 1 mg/L phosphorus limit. The concentration in the main channel opposite the plant has decreased by a factor of three since 1973.
5. The WLSSD discharge was occasionally acutely toxic. It appears that some toxic discharges are related to changes in treatment processes and plant operations in response to special waste treatment needs resulting in high residual chlorine or carbon dioxide concentrations in the effluent. Data indicate that at times the mixtures of the WLSSD plant effluent and bay would be acutely toxic in the immediate vicinity of the discharge pipe but not impact the rest of the bay because of a high dilution ratio.
6. The primary objectives of this research project were not attainable at this site because persistent toxic pollutants were not found in the WLSSD effluent and no persistent open water pollutant problems were apparent.

Water Quality Assessment of St. Louis Bay of Lake Superior

INTRODUCTION

St. Louis Bay of Lake Superior provides a unique opportunity to study a natural ecosystem and related observed response to pollutants to laboratory testing effect endpoints and observations. To understand a pollutant's cause and effect relationship in such a system, it must be studied in sufficient depth to understand the controlling factors. To this end, several on site (field) and laboratory studies were undertaken to quantify possible pollutant impacts and resulting biotic responses of the bay ecosystem.

Such research is needed to provide a basis for the U.S. Environmental Protection Agency's (EPA) Office of Water to provide guidance to the States on the modification of national water quality criteria to site-specific situations, and the control of complex effluents through the National Pollution Discharge System. The EPA Great Lakes National Program Office also needs information on the causes of pollution of St. Louis Bay and the impact of the bay on western Lake Superior.

The primary objectives of this research project were: (1) to field test the EPA guidelines for deriving site specific water quality criteria, (2) to obtain data on the relationship between toxicity testing of a complex effluent and receiving water biotic response, and (3) evaluate the usefulness of water quality criteria to protect a Great Lakes ecosystem.

To meet the above objectives, three conditions must have existed. The first is that a point source discharge to the bay had to be at least chronically toxic, the toxic components of the effluent had to be identified and the bay biota had to be impacted by the effluent. Because the Western Lake Superior Sanitary District (WLSSD) discharge, containing both treated

domestic and industrial wastes, appeared to meet the above conditions, it was selected for initial study. It is the largest single point discharger to the bay; its final effluents had exhibited toxicity in the past and some fish kills had occurred in the embayment near its discharge pipe. During 1982 studies to chemically characterize the WLSSD effluent, determine its toxicity and trace its movement in and out of the bay were initiated while other studies were initiated to provide a water chemistry and biological baseline for the bay from which present and future pollutant impacts on the bay, and the bay's impact on Lake Superior, could be determined. A literature search of all studies relevant to St. Louis Bay was also begun. Information gained from these first year efforts were necessary to determine if the primary objectives of this research project were achievable, and if achievable to plan subsequent studies.

This project was undertaken as a cooperative effort between the U.S. EPA Environmental Research Laboratory-Duluth, University of Minnesota-Duluth, and University of Wisconsin-Superior. Following are reports on individual research tasks undertaken in 1982.

WATER CHEMISTRY
IN
ST. LOUIS BAY
June-November, 1982

(Subtask 1-addendum)

prepared by:

Robert B. Cook

and

John J. Ameel

Lake Superior Basin Studies Center

214 Research Laboratory Building

University of Minnesota, Duluth

Duluth, Minnesota 55812

February 1983

The University of Minnesota is committed to the policy that all persons shall have equal access to its programs, facilities, and employment without regard to race, creed, color, sex, national origin, or handicap.

CONTENTS

Page

List of Tables . . . . . .

List of Figures. . . . . .

Introduction . . . . . .

St. Louis Bay . . . . . .

Sampling Scheme . . . . . .

Methods. . . . . .

Sampling Methods. . . . . .

Analytical Methodos . . . . . .

Results and Discussion . . . . . .

Mixing of WLSSD Effluent with the St. Louis River . .

Nutrient Inputs to St. Louis Bay. . . . . .

Historical Trends . . . . . .

Conclusions. . . . . .

References . . . . . .

Figure Captions. . . . . .

LIST OF TABLES

Page

Table 1. Equivalency of sampling sites . . . . . .

Table 2. Water depths at each sample collection site. .

Table 3. Procedures used for water chemistry analysis .

Table 4. Precision of analytical methods. . . . . .

Table 5. Water chemistry data for samples collected on 16 June 1982 . . . . . .

Table 6. Water chemistry data for samples collected on 7 July 1982 . . . . . .

Table 7. Water chemistry data for samples collected on 20 July 1982. . . . . .

Table 8. Water chemistry data for samples collected on 3 August 1982 . . . . . .

Table 9. Water chemistry data for samples collected on 16 August 1982. . . . . .

Table 10. Water chemistry data for samples collected on 7 September 1982. . . . . .

Table 11. Water chemistry data for samples collected on 21 September 1982 . . . . . .

Table 12. Water chemistry data for samples collected on 5 October 1982. . . . . .

Table 13. Water chemistry data for samples collected on 19 October 1982 . . . . . .

Table 14. Water chemistry data for samples collected on 2 November 1982 . . . . . .

Table 15. Summary of water chemistry data for samples collected June-November 1982 . . . . . .

Table 16. Concentrations of alkalinity, total phosphate, ammonia, and Cl in the WLSSD effluent .

Table 17. Derivation of formula for calculating the mixing of WLSSD effluent with the St. Louis River. . . . . .

Table 18. Compilation of mixing fractions, f, for each of the six embayment sites, for each sampling date . . . . . .

Table 19. Comparison of predicted alkalinity, total phosphorus, and ammonia with the observed mean concentrations in the embayment . . . . .

Table 20. Comparison of inputs to St. Louis Bay from the St. Louis River and WLSSD effluent during 16 June through 2 November 1982 . . . . .

Table 21. Yearly average total phenol concentrations at site L (Interstate-535, Blatnik High Bridge). . . . . .

Table 22. Methods of nutrient analyses used by the five laboratories studying St. Louis Bay . . .

LIST OF FIGURES

Page

Figure 1. The Duluth-Superior Harbor . . . . . .

Figure 2. The Duluth-Superior Inner Harbor (St. Louis Bay) . . . . . .

Figure 3. Total phosphorus at site A (Arrowhead Bridge) between 1972 and 1982. . . . . .

Figure 4. Total phosphorus at site L (Blatnik High Bridge and Burlington Northern Railroad Bridge) between 1972 and 1982. . . . . .

Figure 5. Nitrate/nitrite at site A (Arrowhead Bridge) between 1972 and 1982. . . . . .

Figure 6. Nitrate/nitrite at site L (Blatnik High Bridge and Burlington Northern Railroad Bridge) between 1972 and 1982. . . . . .

Figure 7. Ammonia at site A (Arrowhead Bridge) between 1972 and 1982. . . . . .

Figure 8. Ammonia at site L (Blatnik High Bridge and Burlington Northern Railroad Bridge) between 1972 and 1982. . . . . .

INTRODUCTION

The objective of this study was to characterize the water chemistry of St. Louis Bay with reference to inorganic and organic constituents emitted in the effluent stream of the Western Lake Superior Sanitary District (WLSSD) sewage treatment plant. In this report we present water chemistry data from our study and discuss the influence of the WLSSD effluent stream on water chemistry in St. Louis Bay.

St. Louis Bay

The Duluth-Superior Harbor is comprised of St. Louis Bay, or inner Harbor, the Superior Bay or outer Harbor (Figure 1). The St. Louis River, which flows through the Duluth-Superior Harbor, is the third largest tributary to Lake Superior in terms of area drained and loading of total dissolved solids (Thompson 1978). Average discharge over a 60-year period was 64.3 m^3 sec^{-1} with a range of 2.3 to 1073 m^3 sec^{-1} (MPCA 1977), although average discharge during the present study (June through November 1982) was 116 m^3 sec^{-1} (Minnesota Power, unpub. data).

The Lake Superior seiche also transports water into Superior Bay and St. Louis Bay. The seiche reverses flow in the St. Louis River up to Fond du Lac, the site of the first river dam (Sydor and Stortz 1980). The hydraulic flushing time (Harbor volume ÷ total inflow) for the Harbor was 12 days or 8% per day in 1979; the seiche exchanged 6% per day and the river exchanged 2% per day (Sydor and Stortz 1980). The complex geometry of the Harbor (Figure 1) dictates that little Lake Superior water penetrates

into St. Louis Bay. Also the river flow in 1982 was larger, resulting in a river dominated inner Harbor.

The St. Louis River is the most intensively used tributary to Lake Superior and the Harbor serves as the economic base for the cities of Duluth, Minnesota and Superior, Wisconsin.

The WLSSD sewage treatment plant treats domestic sewage from the cities of Duluth, Cloquet, Carlton, Wrenshall, Scanlon, Hermantown, and Proctor as well as industrial wastes from the Potlach Corporation, a manufacturer of wood products. The plant started operating in 1979; prior to that time domestic wastes were treated at nine separate primary sewage treatment plants (EPA 1975).

The WLSSD effluent discharge pipe (P) extends southwestward from the small split near the WLSSD plant (Figure 2).

Sampling Scheme

For this study we chose 12 sampling sites in St. Louis Bay (Figure 2). Site A (U.S. Highway 2, Arrowhead Bridge) is representative of St. Louis River water entering St. Louis Bay and site L (Interstate-535, Blatnik High Bridge) is representative of water leaving St. Louis Bay. Sites B and C near the Minnesota Power M.L. Hibbard Electric Station are typical of embayments not affected by the effluent from WLSSD.

Sites D through I provide a grid within the embayment receiving WLSSD effluent. Samples taken from this grid will show the spatial distribution of the WLSSD effluent. Site J was chosen to represent an area impacted by a small stream flowing into St.

Louis Bay, as well as by the WLSSD effluent, and site K was chosen to represent an area near the main channel, but somewhat removed from the influence of the WLSSD effluent.

Two separate schemes were used for naming water chemistry and benthos sample collection sites. Six of the water chemistry sites were also used for benthos sample collection. The six water chemistry sites and the corresponding designation for the benthos sample collection sites are presented in Table 1.

METHODS

Sampling Methods

Water samples were collected at the 12 sites in St. Louis Bay (Figure 2) twice a month during the period 16 June through 2 November 1982. Samples for analytes measured in the laboratory were taken at a depth of 1 metre with either a van Dorn or Kemmerer sampling device. Water column depths at each site are presented in Table 2. *In situ* temperature, conductivity, and pH were measured using portable meters; temperature and conductivity were measured at 1 metre depth at each location and field pH was measured at 0.10 metre depth.

Samples for phenol analysis were transferred to glass bottles and were preserved with copper sulfate and phosphoric acid (Standard Methods 1975). Silica and total suspended solid samples were transferred to plastic bottles. Samples for phosphate, alkalinity, and chloride were transferred to glass bottles.

The samples were returned to the lab within 2 hours of collection and kept at 5°C until analysis. Samples for dissolved phosphate and nitrate were filtered through a 0.45 um pre-washed membrane filter upon arrival in the laboratory. Filtered samples were stored in plastic bottles at 5°C until analysis.

Analytical Methods

The analytical methods used in this project are from Standard Methods (1975) or are modifications of the procedures in Standard Methods (1975) and are listed in Table 3. All nutrient samples were analyzed within 24 hours of collection and all

analyses were run within 36 hours. Precision for each method, as estimated from replicate analyses made throughout this study, is presented in Table 4.

Nitrate/nitrite data are incomplete because we encountered unreliable reduction of nitrate to nitrite with pre-packaged reagents. After isolating the cause of the difficulties and purchasing new reagents, we began analyzing for nitrate/nitrite on 7 September 1982.

RESULTS AND DISCUSSION

Conductivity profiles determined at site A and site L (Cook, unpub. data; Jaworski, EPA-Duluth, unpub. data) were vertically homogeneous and indicate that the 1 metre depth is representative of the entire water column.

Conductivity profiles in the small embayment near the WLSSD plant exhibited limited vertical structure (Jaworski, EPA-Duluth, unpub. data). This vertical variation in conductivity was much less than the horizontal variation in conductivity (eg. between sites D and I). Therefore, at any one site in the embayment, the water column can be considered vertically well-mixed relative to the WLSSD effluent.

Water chemistry data for all the sites for each sampling date are presented in Tables 5 through 14. A summary of the water chemistry data, consisting of median and mean values and the range, is presented in Table 15 for each sampling site. Agreement between the median and mean values was good, except in a few instances in which the mean was greater due to a single, large value (eg. TSS at site J and NH_3 at site D).

The primary influence of the WLSSD plant effluent was on alkalinity, total phosphorus, ammonia, and chloride. The concentrations of these parameters in the WLSSD effluent stream (Table 16) were significantly greater than the concentrations in St. Louis Bay.

Water flowing into St. Louis Bay at site A had a chemical composition similar to that at site L, located at the outlet for St. Louis Bay. Notable exceptions were total phosphorus, for

which site L was 12% greater than site A, and chloride, for which site L was two-fold greater than site A.

In addition to being influenced by the St. Louis River and Bay, site L was influenced by the Lake Superior seiche, which mixes Lake Superior water into Superior Bay. The effect of Lake Superior water entering the Duluth-Superior Harbor with the seiche would be to dilute the Harbor water. The importance of the seiche at site L was not determined during this study, although the effect should be small because of the distance between Lake Superior and site L.

The six sites in the embayment receiving the WLSSD effluent (sites D through I) had concentrations of nutrients, alkalinity, and chloride that were greater than the control embayments (sites B and C). The three sites closest to the WLSSD discharge pipe (sites D, E, and F) had concentrations of nutrients, alkalinity, and chloride that were higher than the other three sites in the embayment (sites G, H, and I).

Site J, the site influenced by a small stream, had concentrations of nutrients, alkalinity, and chloride that were similar to sites D through I. Total suspended solids (TSS) at site J, however, were stongly affected by the small stream flowing into the embayment. After heavy rains on the preceding two days, the TSS at site J on 7 July 1982 (Table 6) was ten-fold greater than the median concentration (Table 15). The other six sites in the embayment were not influenced by this small stream, as indicated by the much lower TSS on 7 July (Table 6).

Mixing of WLSSD Effluent with the St. Louis River

The concentrations of nutrients, alkalinity, and chloride at sites D through I are strongly influenced by the effluent from WLSSD. To quantify the extent of this influence we have calculated the mixing of WLSSD effluent with St. Louis River water.

The derivation of the formula for mixing (Table 17) assumes that only two water types - St. Louis River and WLSSD effluent - mix together to produce the embayment water. We used site A (Arrowhead Bridge) for the water composition of the St. Louis River. For the WLSSD effluent we used the concentration of the effluent on the day before our sampling date, and we assumed that the effluent released on that date completely mixed with the embayment within one day. Clearly, mixing in the embayment may take longer than one day or, perhaps, take less time. Mixing is dependent on St. Louis River flow conditions, wind velocity and direction, and WLSSD effluent discharge rate. These parameters are all variable with time of year. In addition, the concentrations of components in the St. Louis River and the WLSSD effluent are not constant during the year.

Despite these limitations in the mixing model, the results obtained are useful for describing the water chemistry patterns in the embayment. In addition, the mixing values allow the results from toxicity tests run on full-strength effluent to be extrapolated to the embayment, in which the effluent is diluted by mixing with river water.

The mixing fraction, f, was determined using chloride. Chloride is conservative (i.e., does not take part in any

biological reactions) and the only source of chloride is from the St. Louis River and the WLSSD effluent. Therefore, the chloride concentrations in the embayment will only be influenced by mixing.

The fraction of WLSSD effluent that mixed with the river ranged from 0.10 to 0.43 for the three sampling sites closest to the effluent discharge pipe (sites D, E, F) and 0.03 to 0.10 for the other three sites (Table 18). Mean values during June to November 1982 were 0.20 to 0.25 for the three sites closest to the effluent discharge pipe and 0.05 to 0.10 for the other sites.

The nutrient elements and alkalinity are non-conservative (i.e., take part in biological reactions) and are affected by both mixing and biological activity. To determine the influence of biological activity we use the mixing fractions (Table 18), along with the St. Louis River and WLSSD effluent concentrations to predict nutrient and alkalinity concentrations in the embayment. When biological uptake takes place the predicted concentration will be greater than the observed. When biological production takes place the predicted concentration is less than the observed.

For alkalinity, the predicted and observed concentrations agree well (Table 19) and indicate no or slight biological modification of this parameter. Biological modification of alkalinity is only important at low values of alkalinity (Cook 1981) or for high levels of biological activity (Goldman and Brewer 1980).

Total phosphorus and ammonia values predicted by the model at sites D, E, and F are less than the observed (Table 19) indicating that total phosphorus and ammonia are produced by biological

activity. The likely source of this production is bacterial activity in the sediments. The bacteria decompose organic matter and liberate the nutrients associated with the organic matter. These nutrients are then transported out of the sediments, either by diffusion or by the movement of invertebrate organisms (eg. tubificids) (Berner 1980). The sediments in the area near sites D, E, and F are relatively rich in organic matter (D. Barlaz, Geology Dept., University of Minnesota, Minneapolis, pers. comm.). This organic matter originated from either the WLSSD sewage treatment plant or from phytoplankton in the embayment, whose growth was stimulated by the nutrients discharged from WLSSD. Biological production of nutrients from the sediments at sites G, H, and I does not appear to be a significant source.

Nutrient Inputs to St. Louis Bay

Another method to quantify the influence of the WLSSD effluent on water chemistry in St. Louis Bay is to make an input budget for the Bay. Comparison of nutrient, alkalinity, and chloride inputs from the St. Louis River and the WLSSD effluent yields information on the relative importance of these two sources.

The concentration measured at site A (Arrowhead Bridge) is representative of the St. Louis River. Discharge at site A was assumed to be 116 m^3 sec^{-1}, the average discharge for this period at Thomson Dam, 30 km upstream (Minnesota Power, unpub. data). No other major rivers nor streams enter the St. Louis River between Thomson Dam and site A. Discharge data for the WLSSD effluent were obtained from Duane Long, WLSSD Plant, Duluth.

A summary of the inputs to St. Louis Bay are presented in Table 20. Even though the average flow rate from WLSSD was two orders of magnitude lower than the St. Louis River flow rate, alkalinity, total phosphorus, and ammonia loadings from WLSSD were 10% of the St. Louis River loadings. Chloride inputs from the two sources were similar with 43% of the total Cl^- input coming from the WLSSD input.

Two other sources of nutrients are not considered in this input budget. The first is the Lake Superior seiche, which transports relatively dilute Lake Superior water into the Duluth-Superior Harbor. The seiche also transports Superior Bay water into St. Louis Bay. The primary influence of the seiche is to dilute St. Louis Bay water and enhance the flushing of the Bay.

The second source not considered in this budget is the transport of nutrients out of the bottom sediments and into the water column of St. Louis Bay. The mixing model (above) showed that sediments were a significant source of ammonia and phosphorus in the small embayment near WLSSD. The sediments in other small embayments in St. Louis Bay may also be a source of nutrients. The loading of nutrients from the sediments was not determined in this study.

A similar nutrient input budget for St. Louis Bay was determined in 1972 (EPA 1975). Comparison of the 1972 and 1982 nutrient input budgets provides information on the influence of the WLSSD plant, which started treating wastes in 1979.

In 1972 the P loading was 8.7×10^5 g day^{-1} of which nearly 50%, or 4.3×10^5 g day^{-1}, was derived from the nine sewage

treatment plants in the area (EPA 1975). During the period June-November 1982, the loading from the WLSSD plant was 0.8 x 10^5g day^{-1} (Table 20) or one-fifth the 1972 value for loading from sewage treatment plants. Thus, the WLSSD sewage treatment plant removes P more efficiently than the treatment plants that preceeded it.

The total P loading rates to St. Louis Bay during 1972 and 1982 were similar (8.7 versus 8.5 x 10^5g day^{-1}, respectively), despite the lower amount of P discharged from sewage treatment plants in 1982. This similarity is due to the high St. Louis River P loading in 1982 (7.6 versus 4.4 x 10^5g day^{-1} in 1972), which in turn is due to the high value for river flow in 1982. The 60 year average for the St. Louis River was 64.3 m^3sec^{-1}, while in 1982 the flow rate was 116 m^3sec^{-1}. Phosphorus concentrations in the St. Louis River were very similar in 1972 and 1982.

The primary conclusion from this budget is that 90% of the ammonia, total phosphorus, and alkalinity entering St. Louis Bay during June to November 1982 were derived from the St. Louis River, from sources upstream of site A (Arrowhead Bridge). Chloride loading from WLSSD and the St. Louis River were approximately equal. The WLSSD effluent causes the mean chloride concentration to increase from 4 mg L^{-1} at site A (Arrowhead Bridge) to 10 mg L^{-1} at site L (Blatnik High Bridge) (Table 15). Although this is a significant increase in chloride concentration, it does not present a problem with respect to water quality. The value of 10 mg L^{-1} is much less than the chloride

concentration in the lower Great Lakes (28 mg L^{-1}; Beeton 1965), and is comparable to values from dilute lakes (Armstrong and Schindler 1971). In addition, the chloride concentration at site L is very similar to the mean chloride concentration of the rivers of the world (Holland 1978).

Historical Trends

To put the data collected during this project in 1982 into historical perspective, we have compiled water chemistry data for St. Louis Bay from other projects for the period 1972 through 1982. The other projects that have comparable data on St. Louis Bay during this period are: Minnesota Pollution Control Agency (MPCA 1978a,b; MPCA 1981); the Western Lake Superior Sanitary District (WLSSD); the Environmental Protection Agency (EPA 1975); the Wisconsin Department of Natural Resources (WDNR 1977); and the Lake Superior BAsin Studies Center Analytical Chemistry Laboratory (LSBSC).

The sites we have chosen for this comparison are site A, at the Arrowhead Bridge (U.S. 53), and site L, at the Blatnik High Bridge (Interstate-535). WLSSD and EPA collected water samples from the Burlington Northern Railroad Bridge, which crosses St. Louis Bay some 500 m upstream from site L (Blatnik High Bridge). The Burlington Northern Railroad Bridge and site L were considered equivalent for this comparison.

If multiple sampling depths were reported for the other studies we chose the 1 metre or shallower sample to correspond to our sampling depth.

Data for total phenol were less complete than for the other parameters and we present only yearly averages for site L (Blatnik High Bridge) in Table 21. Total phenol concentrations decreased from 8 to 9 ug L^{-1} in the mid-1970's to about 3 ug L^{-1} in 1982. The maximum values reported decreased from 20 in 1974 to 5 ug L^{-1} in 1982. The recommended limit for total phenol in surface waters is 100 ug L^{-1}, which was never exceeded at any time in St. Louis Bay.

The five laboratories studying St. Louis Bay used the same analytical method for total phosphorus (Table 22). Four laboratories used the cadmium reduction method for nitrate and three laboratories used the nesslerization method for ammonia (Table 22). A crude comparison of methodology among the five laboratories can be determined when historical data from the laboratories overlaps (Figures 3-8 and discussion below).

The values for total phosphorus, alkalinity, nitrate/nitrite, and ammonia used in this historical comparison are monthly means for each of the laboratories reporting data.

Total phosphorus at site A (Arrowhead Bridge) ranged from 40 to 150 ug L^{-1} over the period 1972-1982 with no historical trend evident (Figure 3).

Total phosphorus at site L (Blatnik High Bridge and Burlington Northern Railroad Bridge) ranged from 30 to 300 ug L^{-1} prior to the 1979 start-up of the WLSSD sewage treatment plant (Figure 4). After 1979 the values ranged from 30 to 140 ug L^{-1}. The effect of the WLSSD sewage treatment plant was to decrease the variability in total phosphorus at site L. The mean value for

total phosphorus between 1972 and 1978 was 110 ug L^{-1} and after 1979 was 75 ug L^{-1}. After the WLSSD plant started operations in 1979 the mean phosphate concentration decreased by 40%. This decrease is significant at the $p \leq 0.05$ level, according to BMDP intervention analysis.

Nitrate/nitrite at site A (Arrowhead Bridge) ranged from 0.010 mg L^{-1} to 0.400 mg L^{-1} during the period 1972 to 1982 with no trend evident (Figure 5). Data from WLSSD were for nitrate only. MPCA data, for which separate nitrate and nitrite values were given, indicated that nitrate/nitrite was 15% greater than nitrate alone.

Nitrate/nitrite at site L (Blatnik High Bridge and Burlington Northern Railroad Bridge) ranged from 0.010 to 1.00 mg L^{-1} prior to 1979 and from 0.10 to 0.380 mg L^{-1} after 1979 (Figure 6). The variability within any one year decreased after 1979. Before the start-up of the WLSSD plant nitrate/nitrite averaged 0.191 mg L^{-1} and after the start-up 0.139 mg L^{-1}.

Ammonia at site A (Arrowhead Bridge) ranged from 0.010 to 0.600 mg L^{-1} between 1972 and 1982 (Figure 7). There are too few data points to verify any trends with time.

Ammonia at site L (Blatnik High Bridge and Burlington Northern Railroad Bridge) ranged from 0.010 to 1.350 mg L^{-1} prior to 1979 and from 0.020 to 0.380 mg L^{-1} after 1979 (Figure 8). Trends with time are difficult to identify for ammonia primarily because prior to September, 1978 the limit of detection for the MPCA data was 0.200 mg L^{-1}, which is much higher than the majority of data points from other sources for this period. On

the basis of the WLSSD data points only the pre-1979 mean ammonia concentration was 0.259 mg L^{-1} and post-1979 mean ammonia concentration was 0.116 mg L^{-1}. Thus there has been a 55% reduction in ammonia concentration since the WLSSD sewage treatment plant started operating in 1979.

CONCLUSIONS

1. At the six sites in the small embayment near the WLSSD plant, ammonia, alkalinity, total phosphorus, and chloride were higher than in the control embayments (sites B and C).

2. The fraction of WLSSD effluent, estimated from chloride concentration, was 0.20-0.25 in the three sites closest to the discharge pipe and 0.05-0.10 in the three sites farthest from the discharge pipe.

3. Ammonia and total phosphorus appear to have a substantial sediment source in the small embayment near WLSSD.

4. Nutrient input budgets for St. Louis Bay revealed that 90% of the alkalinity, ammonia, and total phosphorus loadings were derived from the St. Louis River with the remainder originating from WLSSD. However, high chloride concentrations in the WLSSD effluent contribute 43% of the Cl^- loading to St. Louis Bay, compared to 57% from the St. Louis River.

5. Comparison of the total phosphorus input budget for 1982 with a similar budget for 1972 revealed that the WLSSD sewage treatment plant released one-fifth the total P that was released by the nine sewage treatment plants operating in 1972.

6. Phenol concentrations decreased from 8 to 9 ug L^{-1} in the mid-1970's to 3 ug L^{-1} in 1982.

7. The mean total phosphorus at site L decreased from 110 ug L^{-1} between 1972 to 1979 to 75 ug L^{-1} for 1979 to 1982.

8. The mean ammonia concentration at site L decreased from 0.259 mg L^{-1} (pre-1979) to 0.116 mg L^{-1} after 1979.

REFERENCES

Armstrong, F.A.J. and D.W. Schindler. 1971. Preliminary chemical characterization of waters in the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Canada 28:171-187.

Beeton, A.M. 1965. Eutrophication of the St. Lawrence Great Lakes. Limnol. Oceanogr. 10:240-254.

Berner, R.A. 1980. Early Diagenesis: A Theoretical Approach. Princeton University Press, 237 p.

Cook, R.B. 1981. The biogeochemistry of sulfur in two small lakes. PhD Dissertation. Columbia University, 248 p.

EPA. 1975. Report on St. Louis Bay, Minnesota and Wisconsin. U.S. Environmental Protection Agency, National Eutrophication Survey, Region V, Working Paper No. 123. 43 p.

Goldman, J.C. and P.G. Brewer. 1980. Effect of nitrogen source and growth rate on phytoplankton-mediated changes in alkalinity, Limnol. Oceanogr. 25:352-357.

Holland, H.D. 1978. The Chemistry of the Atmosphere and Oceans. Wiley-Interscience. 351 p.

MPCA. 1977. Study of Minnesota's Tributaries to Lake Superior. Minnesota Pollution Control Agency, Roseville, MN. 87 p.

MPCA. 1978a. Water Quality Sampling Program, Minnesota Lakes and Streams 1970-1975. Vol. 8, Part A and B. Minnesota Pollution Control Agency, Roseville, MN. 1074 p.

MPCA. 1978b. Water Quality Sampling Program, Minnesota Lakes and Streams October, 1975 - September, 1977. Vol. 9, Minnesota Pollution Control Agency, Roseville, MN. 483 p.

MPCA. 1981. Water Quality Sampling Program, Minnesota Lakes and Streams, October, 1977 - September, 1980, Vol. 10. Minnesota Pollution Control Agency, Roseville, MN. 227 p.

Stainton, M.P., M.J. Capael, and F.A.J. Armstrong. 1974. The Chemical Analysis of Fresh Water. Department of Environment, Fisheries and Marine Service: Misc. Spec. Pub. No. 25. Winnipeg, Manitoba. 125 p.

Standard Methods. 1975. Standard Methods for the Examination of Water and Wastewater. 14 Ed. American Public Health Association, Washington, D.C. 1193 p.

Sydor, M. and K. Stortz. 1980. Sources and transports of coal in the Duluth-Superior Harbor. U.S. Environmental Protection Agency, Duluth, MN. Publication number EPA-600/3-80-007. 84 p.

Thompson, M.E. 1978. Major ion loadings to Lake Superior. J. Great Lakes Res. 4:361-369.

WDNR. 1977. Superior Harbor Study, Unpublished Data for 1976-1977. Wisconsin Department of Natural Resources.

Table 1. Equivalency of sampling sites. The water chemistry sampling site in the left column is the same as the benthos sample collection site in the right column.

Water chemistry sampling site designation	Benthos sampling site designation
B	1B
C	2B
F	W1A
G	W1C
H	W2C
K	Interstate

Table 2. Water depths at each sample collection site.

Sample Site	Water Depth (m)
A	7.5
B	2.4
C	2.0
D	2.0
E	2.5
F	3.0
G	2.0
H	2.0
I	4.5
J	2.2
K	1.5
L	8.0

Table 3. Procedures used for water chemistry analysis.

Parameter	Technique
Temperature and Conductivity	Measured *in situ* with a YSI Model 33 Temperature/Conductivity Meter. Calibrated in the laboratory.
Field pH	Measured *in situ* using a Graphic Controls portable pH Meter (model PHM 8100). Calibrated in the field using pH4, 7, and 9 buffers.
Laboratory pH	Measured in the laboratory at room temperature. Beckman Model 3500 Digital pH meter and Sensorex S300C combination electrode. Calibrated with pH 4.0 and 7.0 buffers.
Alkalinity	Titration with sulfuric acid to pH 4.5 and pH 4.2. Standard Methods (1975). pp 278-282.
Dissolved Phosphorus	Filtration through 0.45 um Gelman GN-6 membrane filter. Molybdenum blue/ascorbic acid method. Standard Methods (1975). pp 481-482.
Total Phosphorus	Acid-persulfate digestion followed by molybdenum blue/ascorbic acid analysis. Standard Methods (1975). p 476.
NO_3^-/NO_2^-	Filtration through 0.45 um Gelman GN-6 membrane filter. Cadmium reduction method. Standard Methods (1975) as modified by Stainton, *et al* (1974). pp 42-48.
NH_3	Distillation followed by Nesslerization. Standard Methods (1975). pp 410-415.
Phenol	Distillation, chloroform extraction and formation of antipyrine dye. Standard Methods (1975). pp 577-580.

Table 3 (continued)

Parameter	Technique
Silica	Between 16 June and 22 July 1982 the heteropoly blue method was used. Between 3 August and 2 November 1982, we used metol (p-methylaminophenol sulfate) as the reducing agent. Standard Methods (1975). pp 490-492.
Total Suspended Solids (TSS)	Suspended solids collected on Gelman A-E glass fiber filter disk, dried at 103 C and weighed.
Chloride	Measured using chloride specific ion electrode (Graphics control PHI 91100 Ultra-sensitive Cl^- electrode and Orion Research, Inc. Model 90-02-00 double junction reference electrode).

Table 4. Precision of analytical methods. Precision was estimated from duplicate analyses run during June-November 1982. N is the number of duplicate analyses and precision is the average relative deviation in percent.

Parameter	N	Precision[1] (% S.D.)
pH	29	0.8
Alk	28	0.8
Dis.P	34	1.8
T.P.	37	3.2
NH_3	84	6.7
NO_3^-/NO_2^-	21	3.4
Phenol	7	15.4
Si	36	6.0[2]
	32	0.3[3]
Cl^-	2	7.7

[1] % S.D. = $\frac{\sum_{N}\left[\frac{\text{S.D.}}{\text{mean}}\right]}{N}$ x 100 where N is the number of duplicate analyses.

[2] For the heteropoly blue method used between 16 June and 22 July 1982.

[3] For the metol method used between 3 August and 2 November 1982.

Table 5. Water chemistry data for samples collected on 16 June 1982

Sample Site	Temp. (°C)	Cond. (umho/cm)	Field pH	Lab. pH	Alk (mg/l)	PO_4^{3-} (ugP/l)	TP (ugP/l)	NO_3^-/NO_2^- (ugN/l)	NH_3 (mgN/l)	Phenol (ug/l)	Si (mg/l)	TSS (mg/l)	Cl^- (mg/l)
A	20.1	118	7.54	7.28	49.6	11	92	-	0.15	2	1.4	11	5
B	20.1	112	7.60	7.60	48.5	3	79	-	<0.02	2	1.4	8	5
C	20.0	112	7.97	7.48	46.9	4	79	-	0.10	1	2.1	8	5
D	19.0	200	7.22	7.15	49.7	43	174	-	0.18	1	1.4	16	36
E	19.0	330	6.91	7.03	64.5	80	250	-	0.24	2	2.7	16	52
F	19.0	350	6.60	7.07	60.2	73	270	-	0.24	2	3.4	17	50
G	19.6	142	7.47	7.20	49.0	21	107	-	0.08	1	1.4	8	15
H	17.9	160	6.95	7.19	51.0	28	119	-	0.12	2	1.6	8	23
I	17.9	166	7.28	7.15	51.3	32	130	-	0.13	1	1.4	9	23
J	18.6	231[A]	7.02	7.14	59.5	55	195	-	0.23	3	2.5	26	43
K	19.8	121	7.75	7.30	47.5	16	93	-	<0.02	2	1.6	11	10
L	17.2	129	7.65	7.43	48.0	10	93	-	<0.02	2	2.2	9	9

Table 6. Water chemistry data for samples collected on 7 July 1982

Sample Site	Temp. (°C)	Cond. (umho/cm)	Field pH	Lab. pH	Alk (mg/l)	PO_4^{3-} (ugP/l)	TP (ugP/l)	NO_3^-/NO_2^- (ugN/l)	NH_3 (mgN/l)	Phenol (ug/l)	Si (mg/l)	TSS (mg/l)	Cl^- (mg/l)
A	21.7	135	7.78	7.77	55.5	3	103	-	<0.02	1	1.2	34	3
B	21.6	139	7.67	7.70	56.6	4	53	-	0.03	2	1.2	12	5
C	21.0	139	7.72	7.75	57.1	7	60	-	<0.02	4	1.1	17	5
D	19.9	300	7.53	7.63	99.6	18	150	-	0.58	17	1.6	22	15
E	19.9	365	7.48	7.30	142.6	37	340	-	0.66	25	3.0	23	23
F	19.9	430	7.47	7.68	123.2	57	270	-	0.78	19	2.7	21	20
G	20.0	159	7.71	7.59	61.9	15	92	-	0.16	4	1.9	12	7
H	20.0	157	7.66	7.69	59.6	8	90	-	0.13	3	1.9	14	8
I	20.0	149	7.64	7.66	60.2	11	73	-	0.12	5	2.1	14	6
J	18.2	175	7.62	7.63	63.9	5	100	-	0.23	6	3.7	126	16
K	20.9	139	7.73	7.64	56.3	4	66	-	0.03	2	2.4	16	5
L	20.0	141	7.64	7.67	57.0	7	79	-	0.06	3	1.8	10	8

Remarks: Heavy rain on 5, 6 July.

Table 7. Water chemistry data for samples collected on 20 July 1982

Sample Site	Temp. (°C)	Cond. (umho/cm)	Field pH	Lab. pH	Alk (mg/l)	PO_4^{3-} (ugP/l)	TP (ugP/l)	NO_3^-/NO_2^- (ugN/l)	NH_3 (mgN/l)	Phenol (ug/l)	Si (mg/l)	TSS (mg/l)	Cl^- (mg/l)
A	NS[1]	NS	7.10	7.14	36.6	14	70	-	0.12	3	3.3	12	3
B	NS	NS	7.08	7.30	36.6	13	66	-	0.14	6	3.1	10	3
C	22.1	98	6.61	7.27	36.8	16	71	-	0.13	3	3.0	12	3
D	21.1	210	6.45	6.90	80.8	95	302	-	0.52	8	4.3	19	90
E	22.0	110	6.45	6.68	54.3	45	168	-	0.15	3	3.4	12	52
F	21.0	132	7.15	7.19	39.9	20	87	-	0.22	4	3.2	10	14
G	22.0	106	6.71	7.26	37.0	15	81	-	0.16	3	3.1	11	6
H	21.9	105	6.78	7.16	35.4	16	71	-	0.14	4	3.1	10	10
I	21.5	100	6.69	7.29	36.5	15	78	-	0.15	3	3.3	10	7
J	20.1	120	7.22	7.24	40.2	16	87	-	0.19	3	3.2	9	13
K	22.1	98	6.62	7.31	35.9	13	70	-	0.12	7	3.2	9	4
L	19.9	98	7.15	7.36	37.4	8	148	-	0.50	4	3.0	8	9

[1]NS - not sampled

Table 8. Water chemistry data for samples collected on 3 August 1982.

Sample Site	Temp. (°C)	Cond. (umho/cm)	Field pH	Lab. pH	Alk (mg/l)	PO_4^{3-} (ugP/l)	TP (ugP/l)	NO_3^-/NO_2^- (ugN/l)	pNH_3 (mgN/l)	Phenol (ug/l)	Si (mg/l)	TSS (mg/l)	Cl^- (mg/l)
A	-	98	-	7.22	50.0	41	127	-	0.12	3	3.6	16	4
B	-	98	-	7.40	50.4	47	132	-	0.09	2	3.4	13	4
C	-	100	-	7.52	49.1	28	99	-	0.12	2	3.4	12	4
D	-	353	-	7.27	107.0	143	311	-	0.38	5	3.7	13	65
E	-	331	-	7.39	102.7	139	274	-	0.33	6	3.6	13	65
F	-	408	-	7.13	117.9	185	364	-	0.39	7	3.8	14	79
G	-	110	-	7.55	50.3	32	94	-	0.13	2	2.9	10	10
H	-	113	-	7.52	49.2	28	89	-	0.20	2	2.9	8	8
I	-	111	-	7.52	49.1	36	98	-	0.11	1	2.8	9	7
J	-	114	-	7.40	48.9	78	135	-	0.13	4	2.7	13	8
K	-	103	-	7.56	48.6	60	124	-	0.12	1	2.9	11	6
L	-	109	-	7.38	48.1	24	86	-	0.12	3	2.7	12	6

Table 9. Water chemistry data for samples collected on 16 August 1982

Sample Site	Temp. (°C)	Cond. (umho/cm)	Field pH	Lab. pH	Alk (mg/l)	PO_4^{3-} (ugP/l)	TP (ugP/l)	NO_3^-/NO_2^- (ugN/l)	NH_3 (mgN/l)	Phenol (ug/l)	Si (mg/l)	TSS (mg/l)	Cl^- (mg/l)
A	23.0	135	7.27	6.83	38.4	15	-	-	0.14	<1	3.5	7	6
B	22.9	130	7.44	7.12	47.4	16	-	-	0.13	<1	3.3	7	6
C	23.0	135	7.46	7.37	52.9	22	-	-	0.13	<1	3.4	12	6
D	24.9	490	6.75	7.23	84.5	170	-	-	0.26	3	3.8	11	75
E	24.5	570	6.71	7.15	88.1	214	-	-	0.25	4	3.7	13	78
F	22.8	222	7.07	6.84	52.0	51	-	-	0.16	1	3.2	10	32
G	24.5	264	7.14	7.40	63.1	68	-	-	0.19	<1	3.2	9	34
H	25.0	620	6.59	7.32	91.2	176	-	-	0.27	3	3.6	6	81
I	23.5	245	7.09	7.52	60.3	37	-	-	0.14	1	3.2	9	25
J	24.9	240	7.33	7.39	66.2	29	-	-	0.16	6	3.3	12	32
K	23.8	195	7.15	7.21	51.2	57	-	-	0.13	1	3.2	7	17
L	21.0	135	7.56	7.46	52.6	26	-	-	0.13	2	3.0	7	10

Table 10. Water chemistry data for samples collected on 7 September 1982

Sample Site	Temp. (°C)	Cond. (umho/cm)	Field pH	Lab. pH	Alk (mg/l)	PO_4^{3-} (ugP/l)	TP (ugP/l)	NO_3^-/NO_2^- (ugN/l)	NH_3 (mgN/l)	Phenol (ug/l)	Si (mg/l)	TSS (mg/l)	Cl^- (mg/l)
A	20.2	140	-	7.42	57.0	39	86	83	0.09	4	3.3	10	5
B	20.4	139	-	7.62	58.2	30	75	95	0.09	2	3.0	6	5
C	20.4	139	-	7.64	58.7	33	92	120	0.10	4	3.2	17	5
D	23.4	396	-	7.43	104.6	424	610	86	4.43	3	3.4	13	45
E	23.2	273	-	7.48	83.2	250	357	140	3.18	1	2.9	9	24
F	24.4	200	-	7.54	65.0	94	166	184	0.59	6	2.7	7	17
G	21.0	153	-	7.66	58.8	38	91	129	0.13	1	2.8	5	8
H	21.1	151	-	7.69	58.2	34	86	148	0.13	3	2.7	6	9
I	21.2	152	-	7.64	58.1	40	81	81	0.13	<1	2.7	6	9
J	21.1	171	-	7.61	59.7	48	98	145	0.17	4	2.5	7	12
K	20.6	148	-	7.65	57.5	32	85	147	0.12	<1	2.8	6	8
L	20.5	148	-	7.61	57.6	40	80	132	0.12	2	2.6	5	9

Table 11. Water chemistry data for samples collected on 21 September 1982

Sample Site	Temp. (°C)	Cond. (umho/cm)	Field pH	Lab. pH	Alk (mg/l)	PO_4^{3-} (ugP/l)	TP (ugP/l)	NO_3^-/NO_2^- (ugN/l)	NH_3 (mgN/l)	Phenol (ug/l)	Si (mg/l)	TSS (mg/l)	Cl^- (mg/l)
A	14.2	128	-	7.12	59.3	21	63	127	0.11	1	3.8	6	5
B	14.0	125	-	7.30	58.8	19	173	108	0.10	1	3.3	4	6
C	13.9	128	-	7.33	59.0	18	65	113	0.11	1	3.5	7	5
D	15.0	147	-	7.12	86.1	145	239	54	0.18	2	3.9	10	54
E	15.2	231	-	7.53	74.6	83	160	131	0.17	2	3.5	10	34
F	14.4	158	-	7.38	78.8	108	210	90	0.19	1	3.9	10	44
G	15.0	200	-	7.45	77.0	104	200	91	0.14	2	3.8	7	40
H	14.5	167	-	7.42	67.5	59	134	94	0.15	2	3.5	8	24
I	14.8	158	-	7.16	60.0	35	102	107	0.13	1	3.4	14	13
J	13.9	152	-	7.44	62.8	34	95	135	0.16	7	3.4	6	14
K	14.5	179	-	7.42	63.2	44	136	136	0.15	2	3.5	8	20
L	14.2	140	-	7.49	58.7	30	78	187	0.14	5	2.9	6	12

Table 12. Water chemistry data for samples collected on 5 October 1982

Sample Site	Temp. (°C)	Cond. (umho/cm)	Field pH	Lab. pH	Alk (mg/l)	PO_4^{3-} (ugP/l)	TP (ugP/l)	NO_3^-/NO_2^- (ugN/l)	NH_3 (mgN/l)	Phenol (ug/l)	Si (mg/l)	TSS (mg/l)	Cl^- (mg/l)
A	-	159	-	7.08	58.8	20	70	86	0.15	1	4.2	9	5
B	-	158	-	7.26	58.8	22	74	108	0.14	1	4.1	5	5
C	-	160	-	7.27	59.6	20	79	92	0.14	1	4.2	7	5
D	-	441	-	7.05	89.3	85	193	113	0.37	3	4.4	9	57
E	-	472	-	7.05	92.7	92	212	79	0.40	3	4.6	9	66
F	-	388	-	7.08	82.9	69	174	98	0.28	3	4.4	9	49
G	-	266	-	7.17	71.1	45	127	103	0.24	2	4.2	7	29
H	-	278	-	7.19	70.6	49	133	120	0.19	3	4.1	6	27
I	-	210	-	7.34	64.7	30	92	117	0.17	2	4.0	7	14
J	-	255	-	7.32	69.7	37	111	92	0.15	4	4.3	7	23
K	-	211	-	7.28	64.7	34	91	87	0.21	3	4.0	5	16
L	-	184	-	7.34	62.1	22	85	108	0.15	3	4.0	6	9

Table 13. Water chemistry data for samples collected on 19 October 1982

Sample Site	Temp. (°C)	Cond. (umho/cm)	Field pH	Lab. pH	Alk (mg/l)	PO_4^{3-} (ugP/l)	TP (ugP/l)	NO_3^-/NO_2^- (ugN/l)	NH_3 (mgN/l)	Phenol (ug/l)	Si (mg/l)	TSS (mg/l)	Cl^- (mg/l)
A	8.8	70	-	7.16	31.5	7	61	74	0.04	2	3.6	14	3
B	9.0	69	-	7.22	33.2	11	57	64	0.02	1	3.6	8	3
C	9.1	69	-	7.19	33.8	11	57	65	0.03	3	3.6	7	3
D	11.9	265	-	6.98	83.2	77	208	34	0.13	6	4.5	10	70
E	13.0	340	-	6.99	75.2	77	191	37	0.10	6	4.4	10	60
F	13.2	380	-	7.00	88.8	96	242	20	0.12	5	4.4	9	78
G	11.8	275	-	7.04	70.7	69	185	33	0.13	4	4.3	10	56
H	9.5	101	-	7.21	39.1	19	81	53	0.04	3	3.6	9	11
I	9.2	92	-	7.22	37.3	11	73	61	0.04	3	3.6	11	8
J	10.0	112	-	7.28	44.0	19	70	73	0.05	3	3.8	6	12
K	9.2	68	-	7.25	32.4	10	60	59	<0.02	2	3.6	9	3
L	9.5	80	-	7.26	35.1	12	69	60	0.05	2	3.6	11	5

Table 14. Water chemistry data for samples collected on 2 November 1982

Sample Site	Temp. (°C)	Cond. (umho/Cm)	Field pH	Lab. pH	Alk (mg/l)	PO_4^{3-} (ugP/l)	TP (ugP/l)	NO_3^-/NO_2^- (ugN/l)	NH_3 (mgN/l)	Phenol (ug/l)	Si (mgSi/l)	TSS (mg/l)	Cl^- (mg/l)
A	7.0	82	-	7.34	42.4	13	53	81	0.09	1	3.9	5	4
B	7.0	80	-	7.32	41.0	11	50	88	0.11	2	3.8	4	4
C	7.0	81	-	7.34	41.4	14	51	80	0.11	1	3.8	4	4
D	8.9	182	-	7.21	81.2	168	250	25	0.60	5	4.1	6	62
E	9.5	208	-	7.25	80.4	174	260	39	0.62	3	4.2	6	60
F	8.1	149	-	7.24	83.0	190	270	18	0.43	3	4.2	6	64
G	8.5	168	-	7.26	55.8	53	120	56	0.30	3	3.9	6	31
H	8.0	148	-	7.38	48.6	34	89	39	0.23	2	4.0	6	25
I	8.0	142	-	7.36	48.3	27	95	54	0.19	1	3.8	7	31
J	7.9	158	-	7.36	55.5	34	89	70	0.15	3	4.0	4	25
K	7.2	101	-	7.37	40.4	14	54	77	0.09	2	-	4	12
L	7.6	130	-	7.36	45.5	27	81	83	0.18	1	3.6	6	21

Table 15. Summary of water chemistry data for samples collected June - November, 1982

Sample Site	Conductivity (umho/cm)			Laboratory pH			Alkalinity (mg/l)			Dissolved PO_4^{3-} (ugP/l)		
	Median	Mean	Range	Median	Mean	Range	Median	Mean	Range	Median	Mean	Range
A	128	118	70-159	7.19	7.24	6.83-7.77	49.8	47.9	31.5-59.3	14	18	3-41
B	125	117	69-158	7.31	7.38	7.12-7.70	49.4	49.0	33.2-58.8	14	18	3-47
C	124	116	69-160	7.36	7.42	7.19-7.75	51.0	49.5	33.8-59.6	17	17	4-33
D	282	298	147-490	7.18	7.20	6.90-7.63	85.3	86.6	80.8-107.0	119	137	18-424
E	330	323	110-570	7.20	7.18	6.68-7.53	81.8	85.8	54.3-142.6	88	119	37-250
F	286	282	132-430	7.16	7.22	6.84-7.68	80.8	79.2	52.0-123.2	84	94	20-190
G	164	184	106-275	7.33	7.36	7.04-7.66	60.4	59.5	37.0-77.0	42	46	15-104
H	154	200	101-620	7.35	7.38	7.16-7.69	54.6	57.0	35.4-91.2	34	45	8-176
I	150	152	92-245	7.35	7.39	7.15-7.66	54.7	52.6	36.5-60.3	31	27	11-40
J	164	173	112-255	7.38	7.38	7.14-7.63	59.6	57.0	40.2-69.7	34	36	5-78
K	130	136	68-195	7.34	7.40	7.21-7.65	49.9	49.8	32.4-64.7	24	28	4-60
L	132	129	80-184	7.40	7.44	7.26-7.67	50.4	50.2	35.1-62.1	23	21	8-40

Table 15 (continued)

Sample Site	Total Phosphorus (ugP/l)			Nitrate/Nitrite (ugN/l)			Ammonia (mgN/l)			Phenol (ug/l)		
	Median	Mean	Range	Median	Mean	Range	Median	Mean	Range	Median	Mean	Range
A	71	81	53-127	83	90	81-127	0.12	0.10	<0.02-0.15	2	2	<1-4
B	74	84	50-173	95	93	64-108	0.10	0.08	<0.02-0.14	2	2	<1-6
C	71	73	51-99	92	94	65-120	0.11	0.10	<0.02-0.14	2	2	<1-4
D	239	271	150-610	54	62	25-113	0.38	0.76	0.13-4.43	4	5	1-17
E	250	246	160-357	79	85	37-140	0.29	0.61	0.10-3.18	3	6	1-25
F	242	228	166-364	90	82	18-184	0.26	0.34	0.12-0.78	4	5	1-19
G	107	122	81-200	91	82	33-129	0.15	0.17	0.08-0.24	2	2	<1-4
H	89	99	71-134	94	91	39-148	0.14	0.16	0.04-0.27	3	3	2-4
I	92	91	73-130	81	84	54-117	0.13	0.13	0.04-0.17	1	2	<1-5
J	98	109	70-195	92	103	70-145	0.16	0.16	0.05-0.23	4	4	3-7
K	85	87	54-136	87	101	59-147	0.10	0.12	<0.02-0.21	2	2	<1-7
L	81	89	69-148	108	114	60-187	0.12	0.14	<0.02-0.50	2	3	1-5

Table 15 (continued)

Sample Site	Silica (mgSi/l)			Total Suspended Solids (mg/l)			Chloride (mg/l)		
	Median	Mean	Range	Median	Mean	Range	Median	Mean	Range
A	3.6	3.2	1.2-4.2	10	12	5-34	4	4	3-6
B	3.3	3.0	1.2-4.1	8	8	4-13	5	5	3-6
C	3.4	3.1	1.1-4.2	10	10	4-17	5	4	3-6
D	3.8	3.5	1.4-4.5	12	13	6-22	60	57	15-90
E	3.6	3.6	2.7-4.6	11	12	6-23	56	51	23-66
F	3.6	3.6	2.7-4.4	10	11	6-21	46	45	17-79
G	3.2	3.2	1.4-4.3	8	8	6-12	22	24	6-56
H	3.3	3.1	1.6-4.1	8	8	6-14	16	24	8-81
I	3.0	3.2	1.4-4.0	9	10	6-14	11	14	6-31
J	3.4	3.3	2.5-4.3	8	22	4-126	15	20	8-43
K	3.2	3.0	1.6-4.0	8	9	4-16	9	10	3-20
L	3.0	2.9	1.8-4.0	8	8	5-12	9	10	5-21

Table 16. Concentrations of alkalinity, total phosphate, ammonia, and Cl^- in the WLSSD effluent. Data courtesy of Duane Long, WLSSD.

Date	Alkalinity	Total Phosphorus	Ammonia	Chloride
	(mg L^{-1})			
15 June	200	0.90	1.20	250
6 July	350	0.62	3.00	85
19 July	180	0.48	0.55	205
2 August	220	0.62	<0.10	205
15 August	180	0.48	<0.10	265
6 September	180	1.73	6.20	250
20 September	150	0.96	<0.10	285
4 October	100	0.35	0.66	225
18 October	190	0.55	0.10	250
1 November	220	0.90	1.60	225
Average*	198	0.64	0.56	211

*Volume-weighted average concentrations for the period June-November 1982.

Table 17. Derivation of formula for calculating the mixing of WLSSD effluent with the St. Louis River.

If we assume that the chemical composition in the small embayment near the WLSSD plant is a result of the mixing of Arrowhead Bridge (site A) water with WLSSD effluent water, then the mixing fraction (f) can be calculated from:

$$C = (1-f)\ A + f\ W$$

where:

C = concentration in the embayment

A = concentration at site A (Arrowhead Bridge)

W = concentration of WLSSD effluent

This formula simplifies to

$$f = \frac{C - A}{W - A}$$

For Cl^-, with C = 50 mg L^{-1}, A = 3 mg L^{-1} and W = 250 mg L^{-1} then f is:

$$f = \frac{50 - 3}{250 - 3} = 0.19$$

Therefore, the concentration of Cl^- in the embayment is a result of mixing 19% WLSSD effluent with 81% St. Louis River water.

Table 18. Compilation of mixing fractions, f, for each of the six embayment sites for each sampling date.

Site	6/16	7/7	7/20	8/3	8/16	9/7
D	0.127[a]	0.146[b]	0.431	0.303	0.266[c]	0.163
E	0.192	0.244	0.243	0.303	0.278	0.078
F	0.184	0.207	0.054	0.373	0.100	0.049
G	0.041	0.049	0.015	0.030	0.108	0.012
H	0.073	0.061	0.035	0.020	0.290	0.016
I	0.073	0.037	0.020	0.015	0.073	0.016

	9/21	10/5	10/19	11/2	Average[d]
D	0.175	0.236	0.271	0.262	.256
E	0.104	0.277	0.231	0.253	.227
F	0.139	0.200	0.304	0.271	.198
G	0.125	0.109	0.215	0.122	.097
H	0.068	0.100	0.032	0.095	.097
I	0.029	0.041	0.020	0.122	.048

[a]Effluent values for calculation taken from June 14, 1982.

[b]Effluent values for calculation taken from July 5, 1982.

[c]Plant effluent concentrations taken from August 16, 1982.

[d]Calculated using mean embayment concentration, mean WLSSD effluent concentration, and mean Arrowhead Bridge concentration (Tables 15 and 16).

Table 19. Comparison of predicted alkalinity, total phosphorus, and ammonia, with the observed mean concentrations in the embayment. Arrowhead Bridge (site A) and WLSSD effluent concentrations used to predict the embayment concentrations are also given. All concentrations are in mg L^{-1}.

	Alkalinity		Total Phosphorus		Ammonia	
Site	Predicted	Mean	Predicted	Mean	Predicted	Mean
D	86.3	86.6	.224	.271	.216	.380
E	82.0	85.8	.206	.246	.203	.290
F	77.6	79.2	.191	.228	.190	.260
G	62.4	59.5	.135	.122	.144	.150
H	62.4	57.0	.135	.099	.144	.140
I	55.1	52.6	.108	.091	.121	.130
A		47.9		.081		.100
WLSSD effluent		198		.639		.556

Table 20. Comparison of inputs to St. Louis Bay from the St. Louis River and WLSSD effluent during 16 June - 2 November 1982. The average flow for the St. Louis River is calculated from discharge data at the Thomson Dam, some 30 km upstream from St. Louis Bay. Concentrations used in calculating loadings from the St. Louis River are those measured at site A (Arrowhead Bridge). All average concentrations are volume-weighted averages. The loading is an average loading rate over the 140 day period between 16 June and 2 November 1982.

Source	Average Flow (m^3 sec^{-1})	Alkalinity		Total Phosphorus		Ammonia		Chloride	
		Ave. Conc (mg L^{-1})	Loading (10^7g day^{-1})	Ave. Conc (mg L^{-1})	Loading (10^5g day^{-1})	Ave. Conc (mg L^{-1})	Loading (10^5g day^{-1})	Ave. Conc (mg L^{-1})	Loading (10^7g day^{-1})
WLSSD	1.6	198	2.7	.639	0.88	0.556	0.76	211	2.9
St. Louis River (at site A)	116	46	46	.076	7.6	0.088	8.80	3.9	3.9
Total Loading			49		8.5		9.6		6.8

Table 21. Yearly average total phenol concentrations at site L (Interstate-535, Blatnik High Bridge). Early data are from MPCA (1978a). N is the number of samples collected during the year.

Year	N	Average Total Phenol (mg L^{-1})	Range
1973	1	23	-
1974	15	9.2±6.0	2-20
1975	8	8.0±4.6	4-19
1982	10	2.7±1.2	1-5

Table 22. Methods of nutrient analysis used by the five laboratories studying St. Louis Bay. For details of analytical methods see references in Figures 2 and 3.

Laboratory	Ammonia	NO_3^-/NO_2	Total Phosphorus
LSBSC	Distillation, Nesslerization	Cd Reduction, Azo Dye	Persulfate Digestion, Molybdenum Blue
WLSSD	Phenate	Brucine[3]	Persulfate Digestion, Molybdenum Blue
EPA	Distillation, Nesslerization	Cd Reduction, Azo Dye	Persulfate Digestion, Molybdenum Blue
MPCA	Distillation, Nesslerization[1] Alkaline Oxidation, Diazolization[2]	Cd Reduction, Azo Dye	Persulfate Digestion, Molybdenum Blue
WDNR	Phenate	Cd Reduction, Azo Dye	Persulfate Digestion, Molybdenum Blue

[1] 1972-1977

[2] 1977-1980

[3] NO_3^- only

FIGURE CAPTIONS

Figure 1. The Duluth-Superior Harbor.

Figure 2. The Duluth-Superior Inner Harbor (St. Louis Bay). Locations for water chemistry and plankton sample collection are designated by A through L. P denotes the approximate location of the WLSSD discharge pipe.

Figure 3. Total phosphorus at site A (Arrowhead Bridge) between 1972 and 1982. Depth of sample was $\leq$1 metre. References: LSBSC - this laboratory; WLSSD - Storet computer printout; EPA-EPA (1975); WDNR-WDNR (1977).

Figure 4. Total phosphorus at site L (Blatnik High Bridge and Burlington Northern Railroad Bridge) between 1972 and 1982. Depth of sample was $\leq$1 metre. References as in Figure 3 and: MPCA-MPCA (1978a, b, 1981).

Figure 5. Nitrate/nitrite at site A (Arrowhead Bridge) between 1972 and 1982. Depth of sample was $\leq$1 metre. References as in Figure 3.

Figure 6. Nitrate/nitrite at site L (Blatnik High Bridge and Burlington Northern Railroad Bridge) between 1972 and 1982. Depth of sample was $\leq$1 metre. References as in Figures 3 and 4.

Figure 7. Ammonia at site A (Arrowhead Bridge) between 1972 and 1982. Depth of sample was $\leq$1 metre. References as in Figure 3.

Figure 8. Ammonia at site L (Blatnik High Bridge and Burlington Northern Railroad Bridge) between 1972 and 1982. Depth of sample was $\leq$1 metre. References as in Figures 3 and 4.

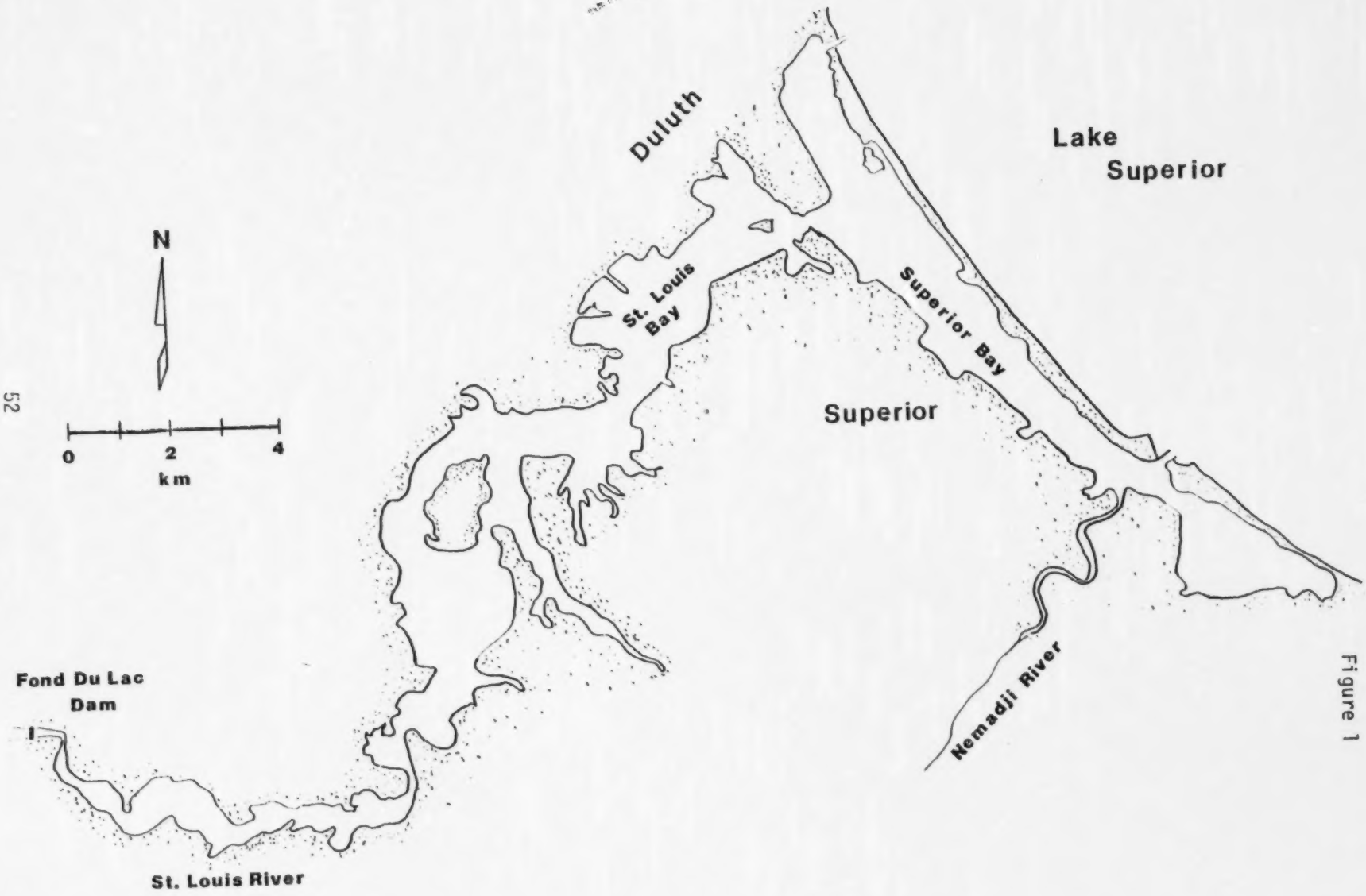

Duluth
Lake
Superior
N
St. Louis
Bay
Superior Bay
Superior
0
2
4
km
Fond Du Lac
Dam
Nemadji River
St. Louis River

Figure 1

Figure 2

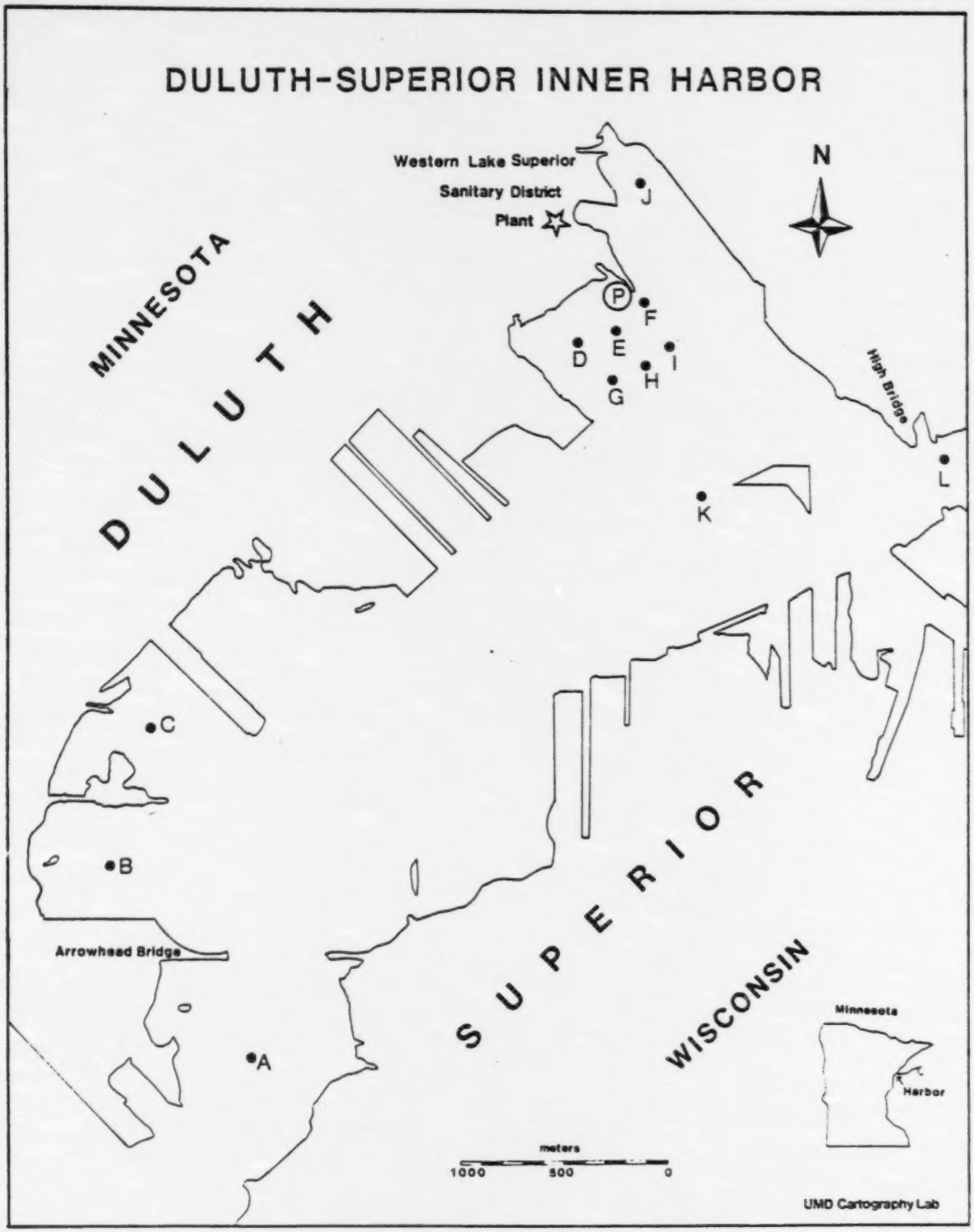

DULUTH-SUPERIOR INNER HARBOR
Western Lake Superior
Sanitary District
Plant
N
MINNESOTA
DULUTH
SUPERIOR
WISCONSIN
High Bridge
Arrowhead Bridge
A
B
C
D
E
F
G
H
I
J
K
L
P
meters
1000
500
0
Minnesota
Harbor
UMD Cartography Lab

Figure 3

TOTAL PHOSPHORUS AT ARROWHEAD BRIDGE

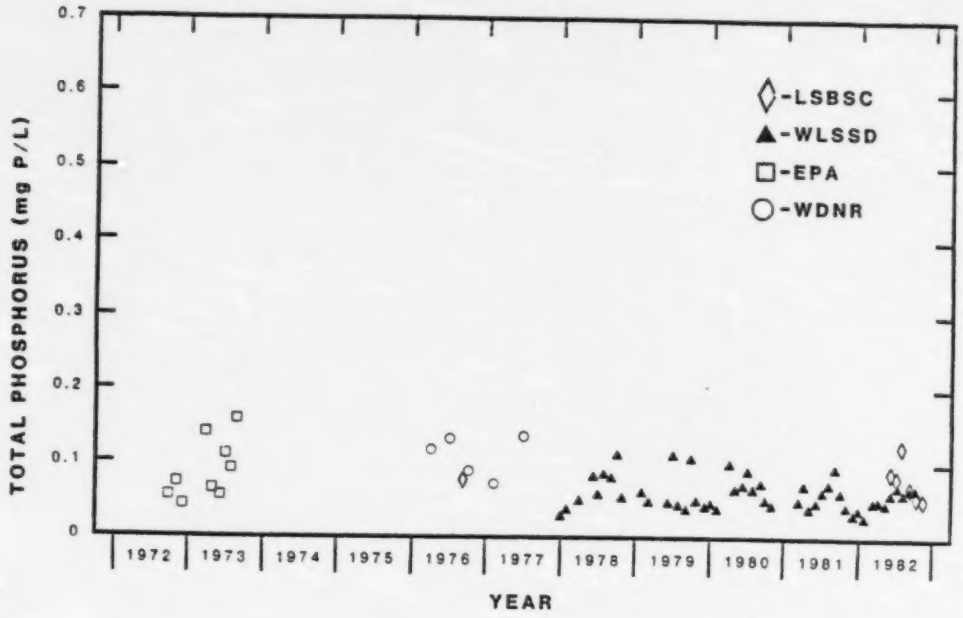


Figure 4

TOTAL PHOSPHORUS AT BLATNIK HIGH BRIDGE

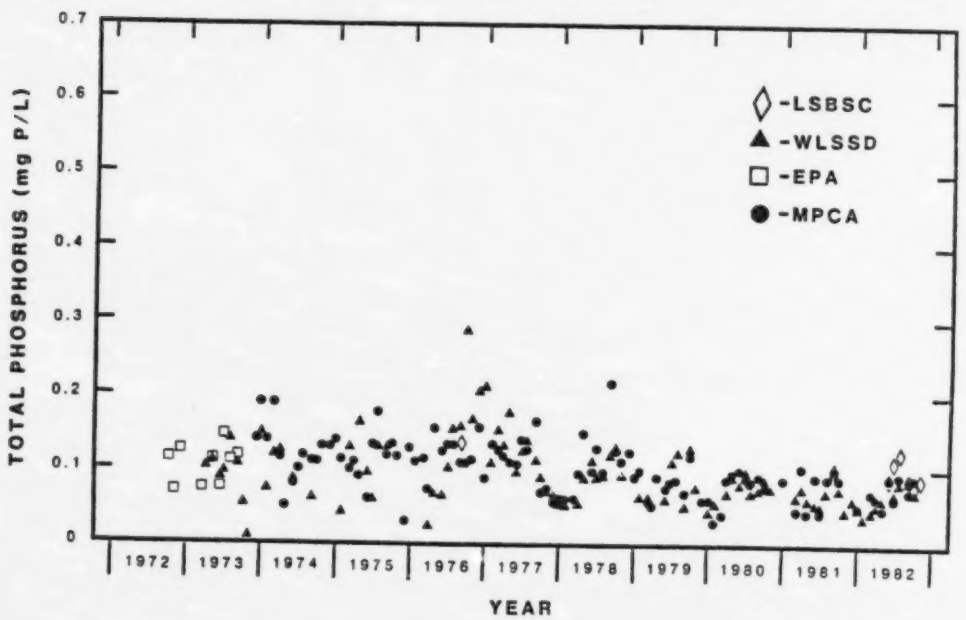


Figure 5

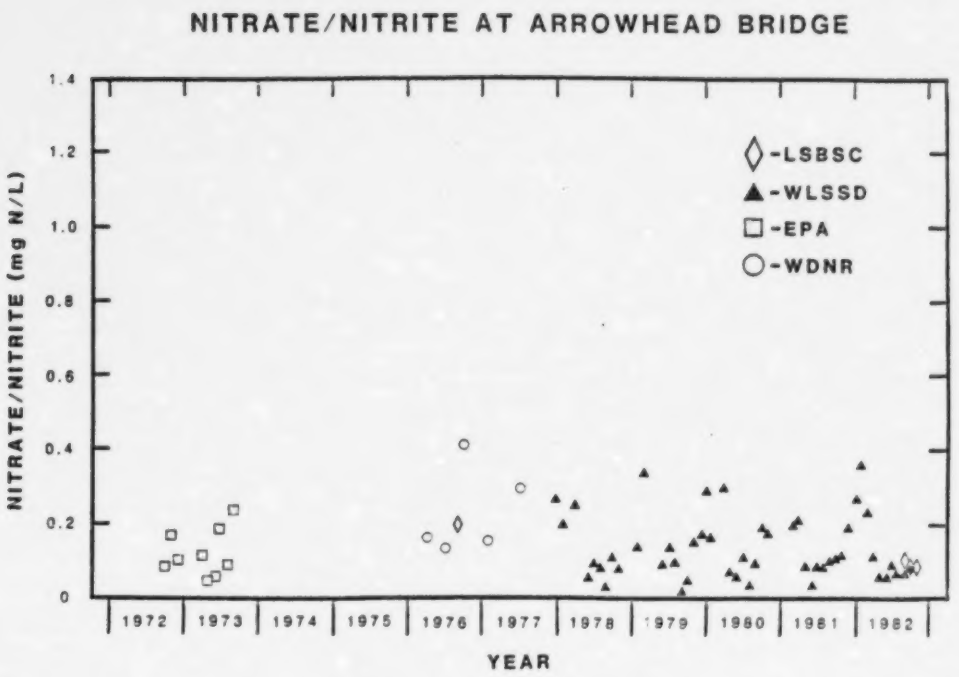


Figure 6

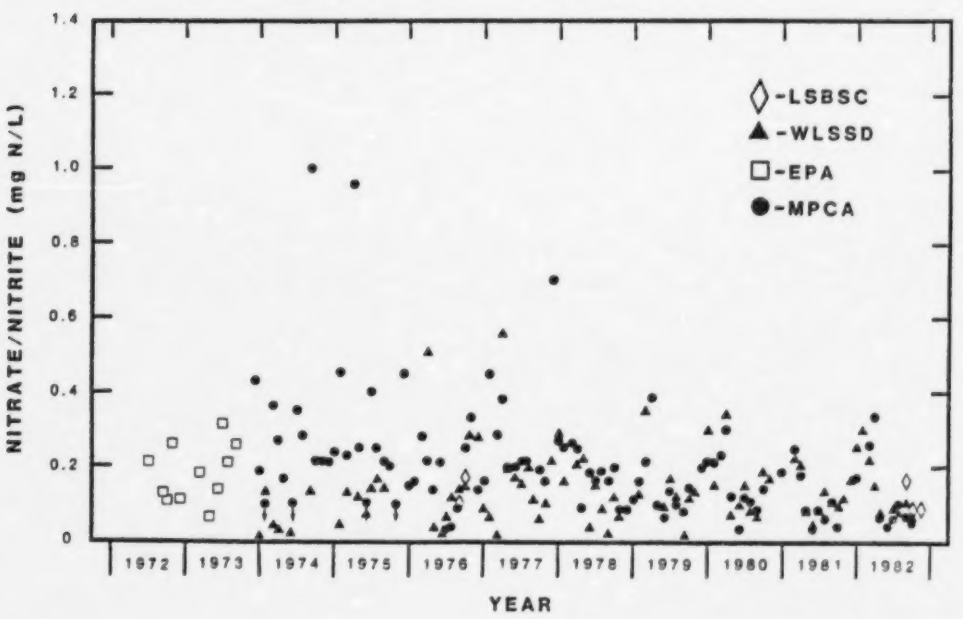


Figure 7

AMMONIA AT ARROWHEAD BRIDGE

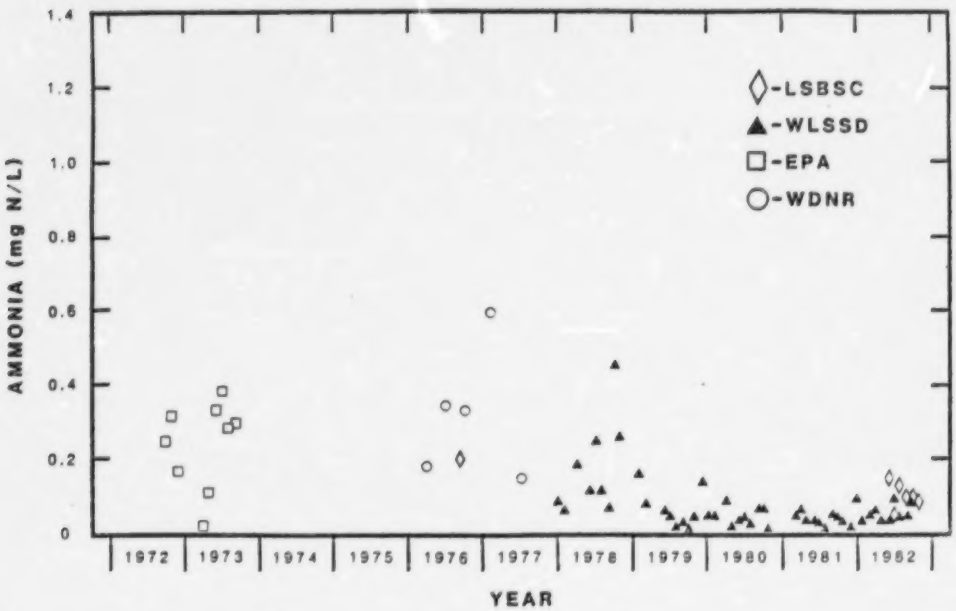
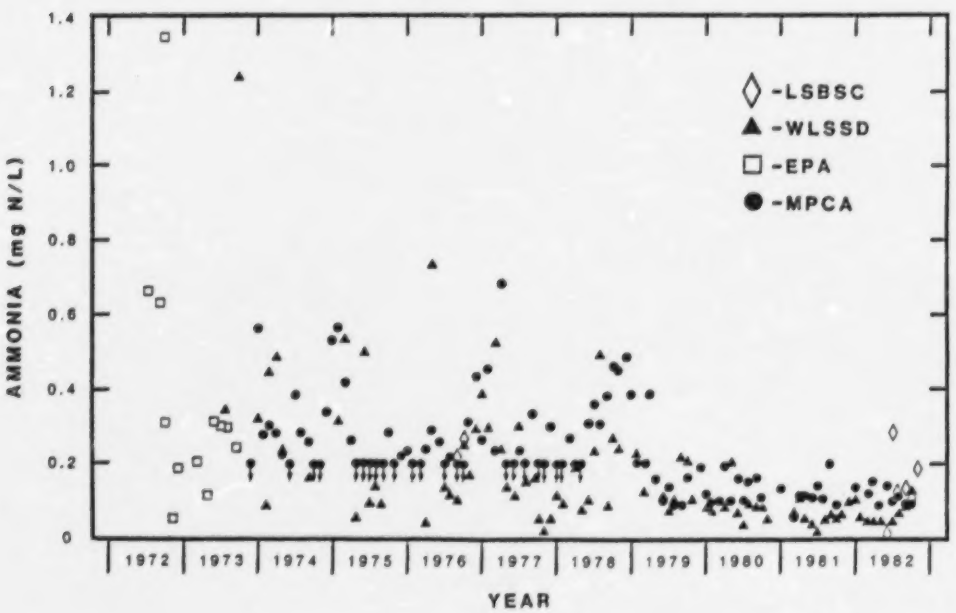


Figure 8

AMMONIA AT BLATNIK HIGH BRIDGE



St. Louis Bay Benthic Macroinvertebrate Survey

by

Thomas Roush

U.S. Environmental Protection Agency

Environmental Research Laboratory-Duluth

6201 Congdon Boulevard

Duluth, Minnesota 55804

December 1982

Introduction

History -- St. Louis Bay has historically experienced very poor water quality conditions. A combination of excess eutrophication presumably due to nutrients from a waste treatment plant, and fish-tainting chemicals, presumably from an upstream paper mill, combined with the modifications of navigational dredging and development of the waterfront have been prime influences for degradation.

The construction of the Western Lake Superior Sanitary District (WLSSD) treatment plant apparently has deviated much of the chemical problems such as low dissolved oxygen and fish tainting chemicals.

Purpose

With the development of WLSSD and its sewage system, a number of waste streams and their chemicals are now processed though the plant and discharged into the lower St. Louis Bay via a diffuser system. The purpose of this survey was to determine the pattern of distribution of the benthic macroinvertebrates in relation to the WLSSD discharge. This survey was conducted in conjunction with a number of other fascets of a study program. Among the other investigations was a survey of the plankton and water quality, and laboratory measures of acute toxicity, test fish responses and chemical determination of contaminants.

Rationale

The benthic macroinvertebrate community was selected for surveying because of their sessile habits and integrating exposure to the environmental conditions in their immediate surroundings. Upstream coves were used as controls since they would not be exposed to chemicals possibly found in the

discharge. Multiple sampling stations were used in order to estimate spatial variation within a cove. The transects in the WLSSD discharge cove were used in order to more precisely delineate the impacted area, if indeed an impact was found. Presumably, if the community was adversly affected, differences in the taxa captured would be found and circumstantially be attributed to the WLSSD discharge. The other investigations would be compared for possible confirmation.

Station Location

Three bays on the Minnesota side of St. Louis Bay were sampled three times during 1983 using mid and quarter-point stations on transects extending across the bays (Figure 1). Upstream bays were near the Arrowhead Bridge. In the WLSSD discharge bay, two 3 station transects were sampled, using the diffuser station as a common point. Sampling was done on June 15, August 10, and October 26, 1982. During August and October, an additional station (INT) southeast of the discharge bay was sampled.

Sampling Regime

Grab samples were taken in discrete triplicates using a 6" x 6" Eckman dredge. The samples were washed in a mesh bottom bucket of 30 mesh screen to remove fine sediments. The residue was placed in labeled jars and preserved with 10% formalin.

Sample Preparation

The samples were washed and deposited in a 9" x 15" white porcelin pan and flooded with a sugar solution to facilitate organism floatation. The organisms, primarily insects, that floated were removed, then the debris was

sorted to remove other organisms. The organisms were re-preserved in 70% ethanol.

Sample Analysis

The organisms were enumerated and identified to convenient taxa using dissecting and compound microscopes. Standard taxonomic reference were utilized.

Results

Tables 2, 3, and 4 present the number of organisms in each taxonomic entity as captured by the combined 3 grabs of the 6" x 6" dredge at each station. Tables 5 and 6 present the summations when all 3 sampling periods are combined, along with simple calculated values relative to clarifying the patterns of distribution. Table 7 presents data by sampling period for total numbers per taxon and percent composition. Table 8 presents the data as density (numbers/m^2) of organisms. Figures 2 and 3 display density and percent composition data.

A total of 105 grab samples captured 2,916 organisms of 22 taxa (18 to 20 each sampling period). 93.4% were oligochaetes and chironomids (90.5 to 96% for individual sampling). Over the three sampling times, 2 to 12 taxa per station were captured. Frequently, the occurrence of a taxon at a station was represented by one individual.

Overall, the upstream bays had the fewest oligochaetes and the largest number of taxa. WIC, the most upstream station in the discharge bay, was quite similar to the upstream bays, possibly due to the direction of the water flow. The station by the diffuser (W1A) showed an increase in the number of taxa during the summer while W2B and W2C remained severely

depressed. The patterns of the upstream stations were reasonably consistent, thus both spacial and temporal differences were in effect.

The oligochaetes were not identified to lower taxonomic entities and the numbers even include a few individuals of the freshwater polychaete, Manayunkia eriensis. Lowest densities were found outside of the discharge bay. The greatest numbers were found in August. This was the most common taxon, comprising 65.9% of all organisms (54.5 to 74.9%, for each sampling).

Chironomids were the second most common group, 27.5% of all organisms (19.1 to 36.1% for each period). Eleven genera were captured, with the most common and widely dispersed being Procladius. Much lower numbers and number of taxa was found in the discharge bay.

Two genera of Trichopera were found. They were more common in the last 2 samplings and a few were found in the discharge bay during October.

Ephemeropera was represented almost exclusively by Hexagenia. None were found in the discharge bay and the October samples contained very small individuals.

Conclusions

The benthic invertebrates demonstrated noticeable differences between the WLSSD discharge bay and two bays upstream.

The discharge bay contained fewer types of organisms.

Table 1. Sampling areas, stations and depth of water (meters) for the 1982 St. Louis Bay, Minnesota, benthos survey.

	June 15	Aug. 10	Oct. 26
1. Transect in the bay south of the Minnesota Power electric generating plant.			
1A - Southern station	2.6	3.2	3.1
1B - Midpoint	2.4	2.5	2.8
1C - Northern station	1.5	3.0	2.2
2. Transect in the bay north of the generating plant.			
2A - Southern point	1.8	2.0	2.5
2B - Midpoint	2.4	2.5	2.5
2C - Northern point	1.5	2.2	2.1
3. Bay receiving WLSSD discharge.			
W1. Southern transect.			
W1A - Close to diffuser	1.5	3.5	3.5
W1B - Midpoint of southern transect	2.1	2.2	2.5
W1C - Close to shipping channel	1.5	2.0	2.7
W2. Northern transect, uses W1A as one end.			
W2B - Midpoint of northern transect	2.7	3.0	2.5
W2C - Close to shipping channel	4.3	4.0	4.3
INT - Southwest of discharge bay	N/A	2.0	2.1

Table 2. Results from the June 1982, sampling of the St. Louis Bay, Minnesota, benthos survey.

Sampling Stations	1A	1B	1C	2A	2B	2C	W1A	W1B	W1C	W2B	W2C	Total
1) Oligochaetes	49	17	3	8	1	2	76	147	71	96	70	540
2) Diptera												
A) Chironomidae												
a) Tanypodinae												
Procladius	20	16	10	17	14	21	3	7	23	4	9	144
Coelotanypus	6	2	10	3	11	3						35
Ablabesmyia	1			1								2
b) Chironominae												
Cryptochironomus stylifera	2	1				1			1			5
Cryptochironomus nais		5		3	1	1		1	6			17
Glyptotendipes	1	2	2	1		2						8
Tanytarsus	1								1			2
Chironomus				3	1	5						9
Polypedilum		5	1	1		1			10		1	19
Micropsectra												
Tribelos												
pupae												
B) Ceratopogonidae												
Palpomia	1			3		1						5
C) Culicidae												
Chaoborus								1				1
3) Tricoptera												
Phylocentropus	1											1
Oecetis	1		2		2							5
4) Ephemeroptera												
Hexagenia	1		2	1	1	2						7
Caenis				1								1
5) Mollusca												
Sphaerium	4			2				1	1			8
6) Amphipoda												
Gammarus fasciatus										1		1
7) Other												
Isopoda											1	1
Hirudinae					2							2

Table 3. Results from the August 1982, sampling of the St. Louis Bay, Minnesota benthos survey.

Sampling Stations	1A	1B	1C	2A	2B	2C	W1A	W1B	W1C	W2B	W2C	INT	Total
1) Oligochaetes	102	34	30	6	22	46	95	109	93	110	196	30	873
2) Diptera													
A) Chironomidae													
a) Tanypodinae													
Procladius	16	4	10	1	11	16	2	31	17	24	25	1	158
Coelotanypus				3		1						1	5
Ablabesmyia	1		1		1								3
b) Chironominae													
Cryptochironomus stylifera				5	1			1	1				8
Cryptochironomus nais	2		2		1	2		11	9			3	30
Glyptotendipes													
Tanytarsus	1								2				3
Chironomus						1			3	1			5
Polypedilum			1						1			1	3
Micropsectra												1	1
Tribelos	1												1
pupae				3				2					5
B) Ceratopogonidae													
Palpomia	1	1			3								5
C) Culicidae													
Chaoborus			1			1							2
3) Tricoptera													
Phylocentropus	11		3	7	4	6		1				1	23
Oecetis													
4) Ephemeroptera													
Hexagenia	1	2	1		2	1							7
Caenis													
5) Mollusca													
Sphaerium			1	2	2				1			2	8
6) Amphipoda													
Gammarus fasciatus					2	1	1						4
7) Other													
Isopoda													
Hirudinae	2		4			2		1				2	11

Table 4. Results from the October 1982, sampling of the St. Louis Bay, Minnesota benthos survey.

Sampling Stations	1A	1B	1C	2A	2B	2C	W1A	W1B	W1C	W2B	W2C	INT	Total
1) Oligochaetes	56	23	12	15	4	25	74	93	78	35	84	11	510
2) Diptera													
A) Chironomidae													
a) Tanypodinae													
Procladius	20	4	3		1	8	35	19	67	42	43	10	252
Coelotanypus	5		5	2	1	6			5			5	29
Ablabesmyia	1	3											4
b) Chironominae													
Cryptochironomus stylifera				1	2	2	1	1	2				9
Cryptochironomus nais						1							1
Glyptotendipes					1								1
Tanytarsus			1				1						2
Chironomus		1	2	1	3	2	22	1					32
Polypedilum		1		2					4		1	1	9
Micropsectra													
Tribelos													
pupae													
B) Ceratopogonidae													
Palpomia	1		2										3
C) Culicidae													
Chaoborus	2						3					1	6
3) Tricoptera													
Phylocentropus	3	7	2	2	1	2	1	1	1				20
Oecetis			1										1
4) Ephemeroptera													
Hexagenia	2	5	13	1	2	1						8	32
Caenis					1								1
5) Mollusca													
Sphaerium		1		1					7				9
6) Amphipoda													
Gammarus fasciatus							2	8			1		11
7) Other													
Isopoda													
Hirudinae	4			1		1							6

Table 5. Summary results of the 3 samplings of the 1982 St. Louis Bay, Minnesota benthos survey.

Sampling Stations	1A	1B	1C	2A	2B	2C	W1A	W1B	W1C	W2B	W2C	INT	Total
1) Oligochaetes	207	74	45	29	27	73	245	349	242	241	350	41	1923
2) Diptera													
A) Chironomidae													
a) Tanypodinae													
Procladius	56	24	23	18	26	45	40	57	107	70	77	11	554
Coelotanypus	11	2	15	8	12	10			5			6	69
Ablabesmyia	3	3	1	1	1								9
b) Chironominae													
Cryptochironomus stylifera	2	1		6	3	3	1	2	4				22
Cryptochironomus nais	2	5	2	3	2	4		12	15			3	48
Glyptotendipes	1	2	2	1	1	2							9
Tanytarsus	2		1				1		3				7
Chironomus		1	2	4	4	8	22	1	3	1			46
Polypedilum		6	2	3		1			15		2	2	31
Micropsectra												1	1
Tribelos	1												1
pupae				3				2					5
B) Ceratopogonidae													
Palpomia	3	1	2	3	3	1							13
C) Culicidae													
Chaoborus	2		1					4	1			1	9
3) Tricoptera													
Phylocentropus	15	7	5	9	5	8	1	2	1			1	54
Oecetis	1		3		2								6
4) Ephemeroptera													
Hexagenia	4	7	16	2	5	4						8	46
Caenis				1	1								2
5) Mollusca													
Sphaerium	4	1	1	5	2			1	9			2	25
6) Amphipoda													
Gammarus fasciatus					2	1	3	8		1	1		16
7) Other													
Isopoda											1		1
Hirudinae	6		4	1	2	3		1				2	19

Table 6. Summary of the number of taxa and organisms and percent composition of two major taxa from the 1982 St. Louis Bay, Minnesota, benthos survey.

Sampling Stations	1A	1B	1C	2A	2B	2C	W1A	W1B	W1C	W2B	W2C	INT	Total
Number of Taxa	16	13	16	15	16	13	7	10	11	4	5	11	22
Number of Organisms	320	134	125	97	98	163	313	439	405	313	431	78	2916
% Oligochaetes	64.7	55.2	36.0	29.9	27.6	44.8	78.3	79.5	59.8	77.0	81.2	52.6	65.9
% Oligochaetes + Procladius	82.2	73.1	54.4	48.5	54.1	72.4	91.1	92.5	86.2	99.4	99.1	66.7	84.9

Table 7. Numbers of organisms and percent composition, by sampling period, for the 1982 St. Louis Bay, Minnesota, benthos survey.

	June		August		October		Total	
	No.[1]	%	No.	%	No.	%	No.	%
1) Oligochaetes	540	66.4	873	74.9	510	54.5	1923	65.9
2) Diptera								
A) Chironomidae								
a) Tanypodinae								
Procladius	144	17.7	158	13.6	252	26.9	554	19.0
Coelotanypus	35	4.3	5	0.4	29	3.1	69	2.4
Ablabesmyia	2	0.2	3	0.3	4	0.4	9	0.3
b) Chironominae								
Cryptochironomus stylifera	5	0.6	8	0.7	9	1.0	22	0.8
Cryptochironomus nais	17	2.1	30	2.6	1	0.1	48	1.6
Glyptotendipes	8	1.0			1	0.1	9	0.3
Tanytarsus	2	0.2	3	0.3	2	0.2	7	0.2
Chironomus	9	1.1	5	0.4	32	3.4	46	1.6
Polypedilum	19	2.3	3	0.3	9	1.0	31	1.1
Micropsectra			1	0.1			1	T
Tribelos			1	0.1			1	T
pupae			5	0.4			5	0.2
B) Ceratopogonidae								
Palpomia	5	0.6	5	0.4	3	0.3	13	0.4
C) Culicidae								
Chaoborus	1	0.1	2	0.2	6	0.6	9	0.3
3) Tricoptera								
Phylocentropus	1	0.1	33	2.8	20	2.1	54	1.9
Oecetis	5	0.6			1	0.1	6	0.2
4) Ephemeroptera								
Hexagenia	7	0.9	7	0.6	32	3.4	46	1.6
Caenis	1	0.1			1	0.1	2	T
5) Mollusca								
Sphaerium	8	1.0	8	0.7	9	1.0	25	0.9
6) Amphipoda								
Gammarus fasciatus	1	0.1	4	0.3	11	1.2	16	0.5
7) Other								
Isopoda	1	0.1					1	T
Hirudinae	2	0.2	11	0.9	6	0.6	19	0.7
Total	813		1165		938		2916	
No. Taxa	20		18		19		22	

[1] No. = number

Table 8. Density (numbers/m^2) of benthic macroinvertebrates collected during 1983 from St. Louis Bay, Minnesota.

	1A	1B	1C	2A	2B	2C	W1A	W1B	W1C	W2B	W2C	INT
1) Oligochaetes	989	354	215	139	129	349	1171	1668	1157	1152	1673	294
2) Diptera												
A) Chironomidae												
a) Tanypodinae												
Procladius	268	115	110	86	124	215	191	272	511	335	368	79
Coelotanypus	53	10	72	38	57	48			24			43
Ablabesmyia	14	14	5	5								
b) Chironominae												
Cryptochironomus stylifera	10	5		29	14	14	5	10	19			
Cryptochironomus nais	10	24	10	14	10	19		57	72			22
Glyptotendipes	5	10	10	5	5	10						
Tanytarsus	10	5					1		14			
Chironomus		5	10	19	19	38	105	5	14	5		
Polypedilum		29	10	14		5			72		10	15
Micropsectra												7
Thibeles	5											
Pupae				14				10				
B) Ceratopogonidae												
Palpomia	14	5	10	14	14	5						
C) Culicidae												
Chaoborinae												
Chaoborus	10		5			5	14	1				7
3) Tricoptera												
Phylocentropus	72	33	24	43	24	38	5	10	5			7
Oecetis	5		14		10							
4) Ephemeroptera												
Hexaginia	19	33	76	10	24	19						62
Caenis				5	5							
5) Mollusca												
Sphaerium	19	5	5	24	10			5	43			14
6) Amphipoda												
Gammarus fasciatus					10	5	14	38		5	5	
7) Other												
Isopoda											5	
Hirudinae	29		19	5	10	14		5				14
Number of taxa	16	13	16	15	15	14	8	10	10	4	5	11
Density of organisms	1531	641	598	464	464	785	1512	2086	1933	1497	2062	538

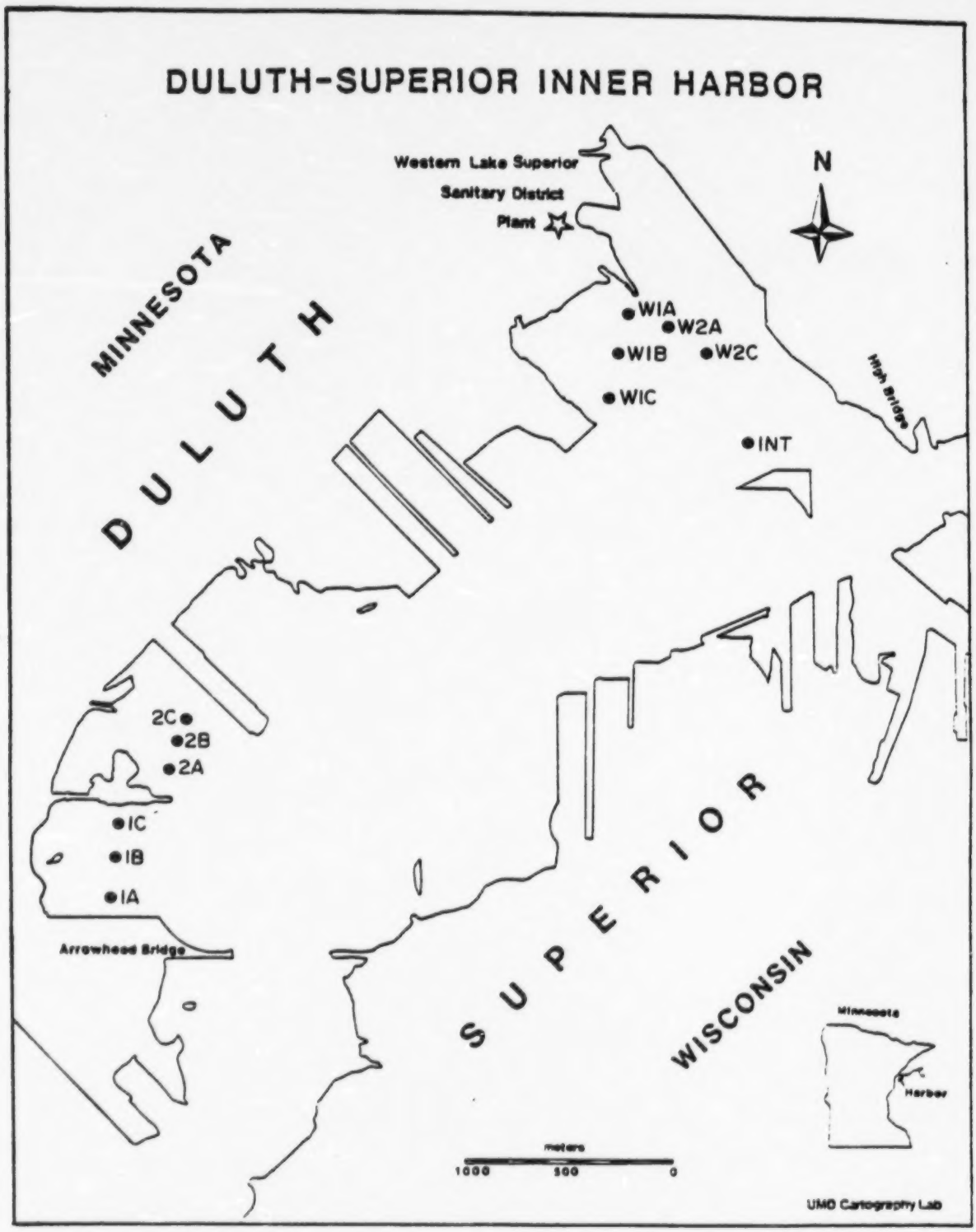


Figure 1. Sampling stations for the 1982 benthos survey of St. Louis Bay, Minnesota.

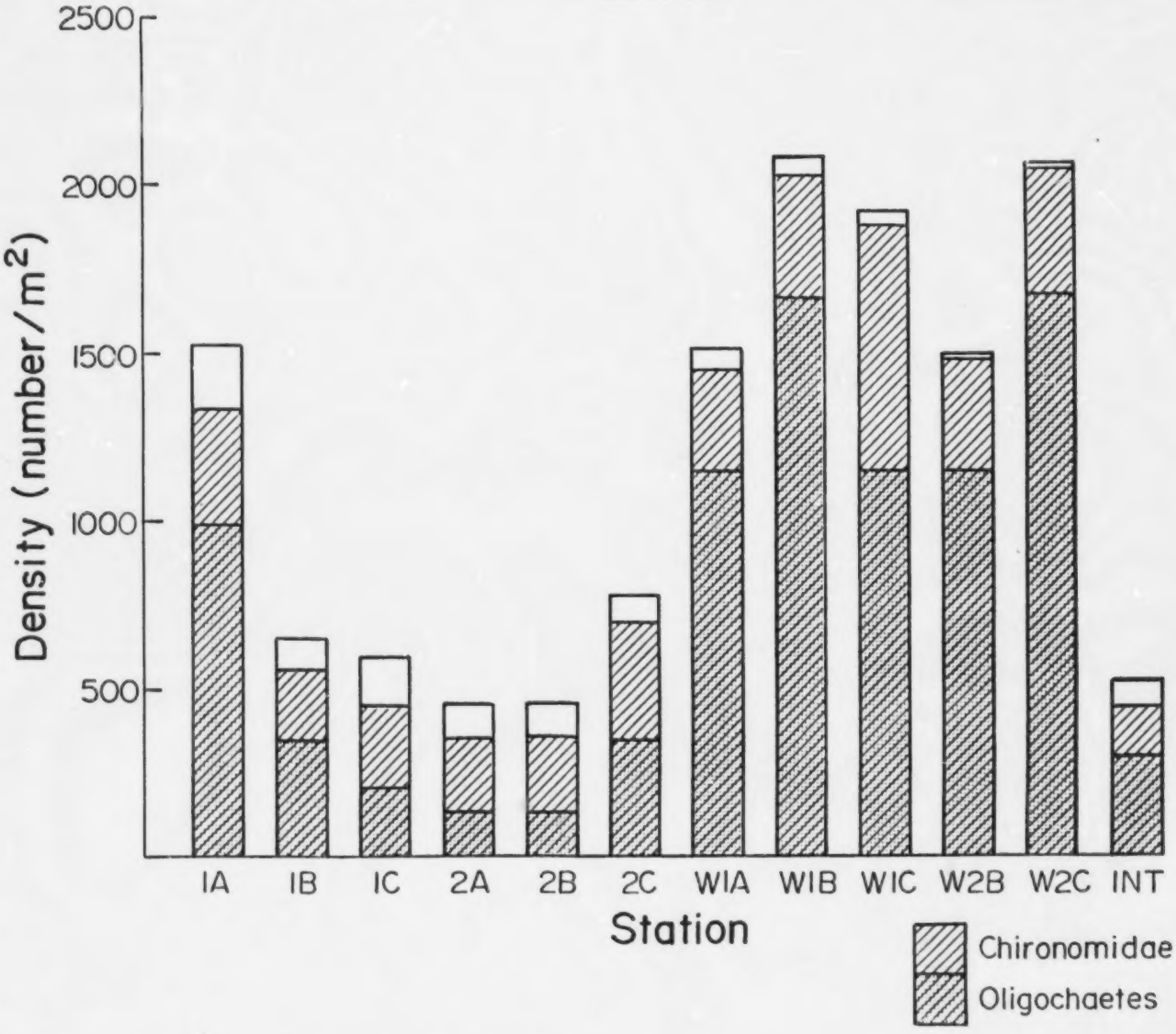


Figure 2. Density (no./m^2) of benthic macroinvertebrates collected during 1983, St. Louis Bay, Minnesota.

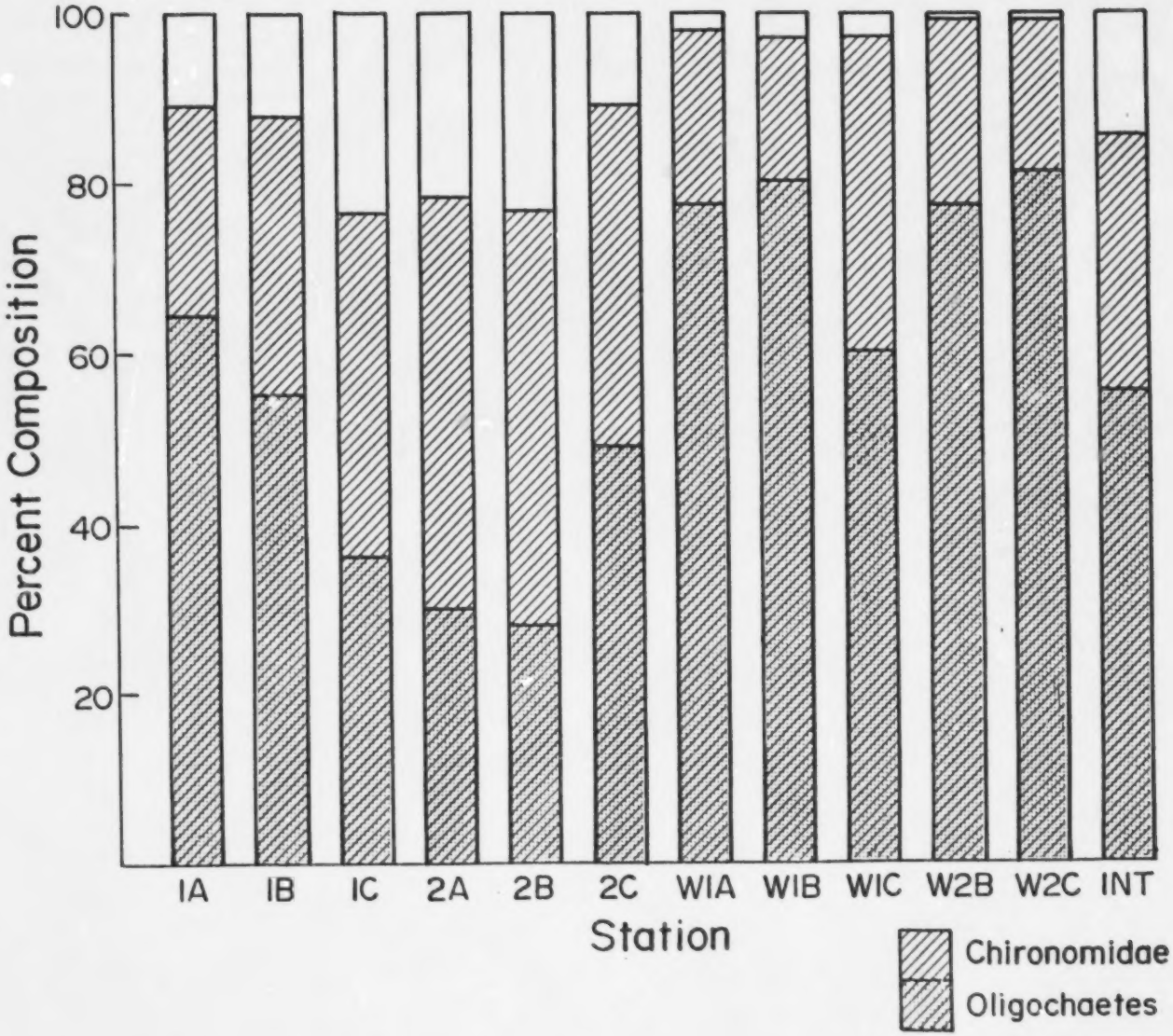


Figure 3. Percent composition of benthic macroinvertebrates collected during 1983, St. Louis Bay, Minnesota.

SEASONAL PRIMARY PRODUCTION AND PLANKTON DYNAMICS IN THE ST. LOUIS RIVER AND HARBOR

(Subtask 3)

prepared by:
Jack R. Hargis
Department of Biology

Lake Superior Basin Studies Center
214 Research Laboratory Building
University of Minnesota, Duluth
Duluth, Minnesota 55812

January, 1983

The University of Minnesota is committed to the policy that all persons shall have equal access to its programs, facilities and employment without regard to race, creed, color, sex, national origin or handicap.

CONTENTS

Page

List of Figures and Tables . . . . . .

Purpose. . . . . .

Materials and Methods. . . . . .

Results and Discussion

Phytoplankton . . . . . .

Zooplankton . . . . . .

Literature Cited . . . . . .

LIST OF FIGURES AND TABLES

Page

FIGURE 1. Sample Locations for Water Chemistry and Plankton Subtasks . . . . . .

TABLE 1. Phytoplankton List for Duluth - Superior Harbor Study, 1982 . . . . . .

TABLE 2a. June Phytoplankton in the Duluth - Superior Harbor, 1982. . . . . .

TABLE 2b. July Phytoplankton in the Duluth - Superior Harbor, 1982. . . . . .

TABLE 2c. August Phytoplankton in the Duluth - Superior Harbor, 1982. . . . . .

TABLE 3. Chlorophyll a Concentrations from the Duluth - Superior Harbor, Summer, 1982 (ug/liter). . . . . .

TABLE 4. Composite List of Zooplankton from Six Sites in the Duluth - Superior Harbor, Summer, 1982 . . . . . .

TABLE 5. Volumes Filtered in Zooplankton Collection (liters) at Six Sites in the Duluth - Superior Harbor during Summer, 1982. . . . . .

TABLE 6a. June Zooplankton in the Duluth - Superior Harbor, 1982 (no. per liter) . . . . . .

TABLE 6b. July Zooplankton in the Duluth - Superior Harbor, 1982 (no. per liter) . . . . . .

TABLE 6c. August Zooplankton in the Duluth - Superior Harbor, 1982 (no. per liter) . . . . . .

PURPOSE

The purpose of this subtask was to document the distribution of plankton organisms within the Duluth - Superior Harbor, relative to the effluent of the Western Lake Superior Sanitary District (WLSSD). Samples of phytoplankton and zooplankton were collected from six sites in the Harbor: two sites were within the bay where WLSSD effluent is discharged (coded E and H); two sites were chosen to match these in bays "upstream" and north and south of the Minnesota Power & Light Company plant (C and B, respectively); the fifth and sixth sites were located at the Arrowhead Bridge (A) and the High Bridge (L). These last two sites are located where plankton organisms would be well-mixed "upstream" (A) and "downstream" (L) relative to conditions within the WLSSD Bay.

MATERIALS AND METHODS

Samples were collected at two-week intervals at each site, coordinated with the water quality sampling subtask (Figure 1). Phytoplankton were taken from the upper meter of water by VanDorn water sampler. Slides were made following McNabb (1960); 15 ml of the Lugol preserved sample were filtered onto a millipore filter using a pressure - vacuum pump at low vacuum. The filters were placed on a drop of immersion oil and left to stand overnight, until clear. A drop of Permount solution (Fisher Scientific) was placed on top of the filter and covered with a cover slip.

Six slides were made for each sampling period - one for each of the six sites. The slides were counted at 400X, using random fields. About 50 fields were counted to give a total of 200 individuals counted per slide. The number of fields varied with the density of organisms on the slides. Individuals were identified to genus, and to species where possible. All

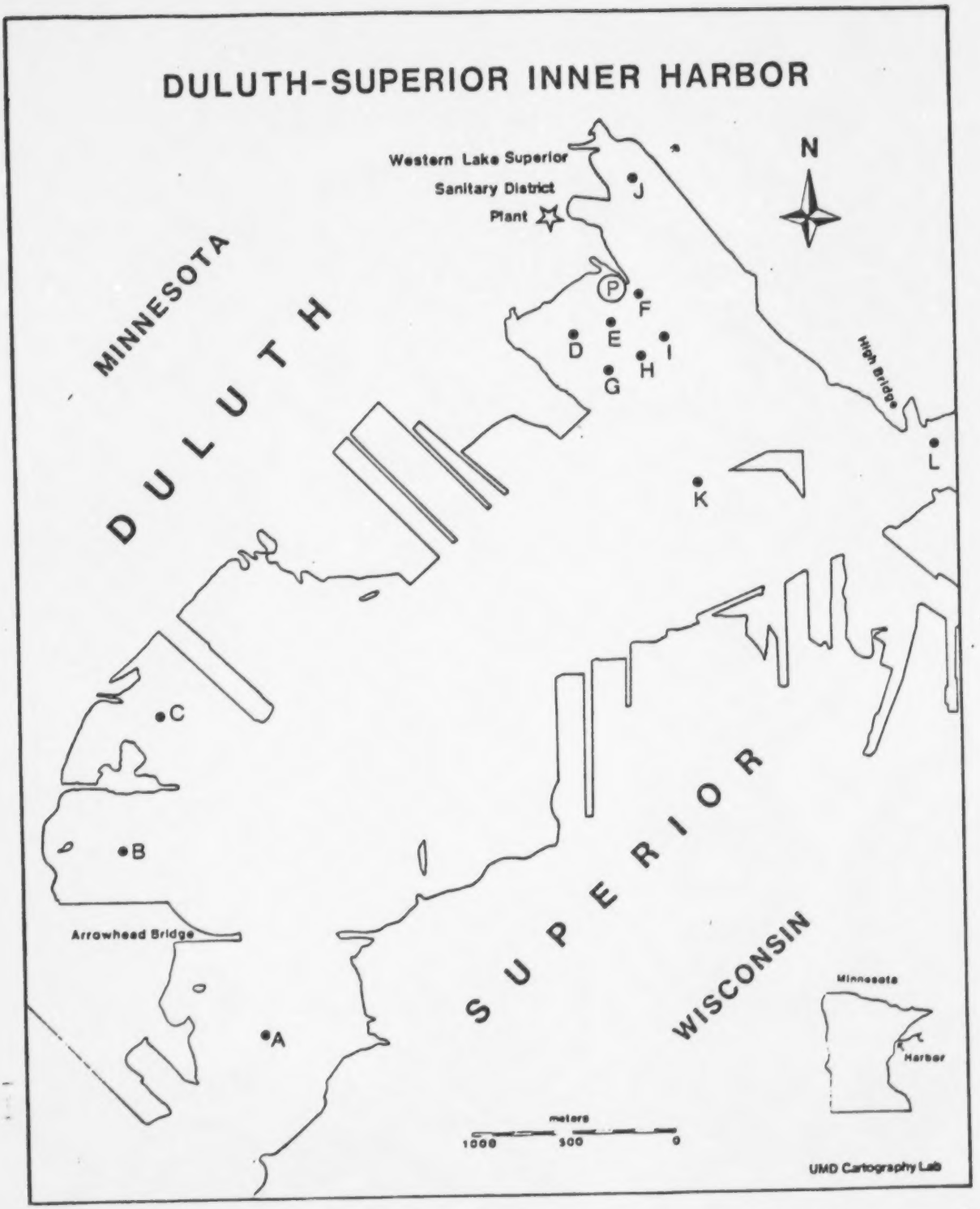


Figure 1. Sample Locations for Water Chemistry and Plankton Subtasks.

the colonies were counted as a single unit. Filaments were counted only if 5 or more cells appeared in the field of view. Chlorophyll a concentrations from each sample were measured by fluorometer (Strickland and Parsons, 1972), corrected for background fluorescence. All values were read from standard curves derived from purified chlorophyll a (Sigma Chemical Company). Zooplankton were taken by vertical tows at each site with a standard, 80μ mesh Wisconsin net. Preservation in 4% formalin plus 60 g/liter sucrose was used for the triplicate samples taken each time. Zooplankton were counted in open chambers according to the procedures recommended by the International Biological Programme (Edmondson and Winberg, 1971); three hundred organisms, minimum, were counted at each site. Edmondson (1959) and Pennak (1978) were used for taxonomic reference.

RESULTS AND DISCUSSION

The Duluth - Superior Harbor supports a relatively rich assemblage of phytoplankton during summer. Thirty-three species were identified along with twenty more units identified to genus (Table 1). Only twelve species (units) were found in large enough numbers to be considered common. There were not anomalies in distribution or densities of these common species between control sites and sites near the outflow of WLSSD (Table 2a-c), except an increase in the density of Cryptomonas erosa in the proximity of the effluent is indicated. Diatoms tended to decline as the summer progressed and waters warmed (Stephanodiscus, Synedra), as is common (Fogg, 1975). Green algae fluorished in the warmer waters and, surprisingly, very few blue-green algae appeared. The low light intensities in the brown harbor waters may favor the growth of greens over blue-greens, barring any organic pollution or nitrogen limitation (Wetzel, 1975).

Table 1. Phytoplankton List for Duluth-Superior Harbor Study, 1982.

Bacillariophyceae (diatoms)
- Achnanthes lanceolata var. rostrada
- Asterionella formosa *
- Cocconeis spp.*
- Coscinodiscus spp.
- Cyclotella Meneghiniana*
- Cymbella spp.
- Diatoma himenale
- Diatoma spp.
- Eunotia pectinalis
- Fragilaria capucina
- Fragilaria crotonensis
- Fragilaria spp.
- Gomphonema spp.
- Melosira distans*
- Melosira granulata*
- Melosira varians
- Melosira spp.*
- Meridion circulare
- Navicula cuspidata
- Navicula exigua
- Navicula gastrum
- Navicula hungarica
- Navicula pupula
- Navicula radiosa
- Navicula viridula
- Navicula spp.*
- Nitzschia palea
- Nitzschia tryblionella
- Nitzschia spp.
- Pinnularia spp.
- Rhoicosphenia curvata
- Stauroneis crucicula
- Stephanodiscus spp.*
- Synedra actinastroides
- Synedra ulna*
- Synedra spp.*
- Tabellaria fenestrata
- unidentified diatoms

Chlorophyta (green algae)
- Actinastrum spp.
- Ankistrodesmus
- Cosmarium
- Crucigenia quadrata
- Elaktothrix viridis
- Kirchneriella lunaris
- Pandorina morum
- Pediastrum duplex
- Scenedesmus spp.*
- unidentified unicells
- unidentified colonies
- unidentified filaments

Cyanophyta (blue-green algae)
- Anabaena spp.
- Anacystis spp.
- Aphanocapsa spp.

Euglenophyta
- Euglena spp.
- Phacus longicauda

Pyrrophyta
- Ceratium hirudinella

Cryptomonadales
- Cryptomonas erosa*

* Common species throughout study.

Table 2a. June Phytoplankton in the Duluth-Superior Harbor, 1982.

Species	Sites					
	A	B	C	E	H	L
Asterionella formosa	467*	733	800	600	1067	933
Cocconeis spp.	200	133	133	200	133	67
Cyclotella meneghiniana	1267	733	600	400	400	400
Melosira distans	1533	933	1867	2400	1867	2000
Melosira granulata	3467	3933	4600	3267	4000	4200
Melosira spp.	0	200	867	0	800	133
Navicula spp.	400	600	600	267	400	267
Stephanodiscus spp.	1533	533	1400	533	667	267
Synedra ulna	333	67	200	200	67	133
Synedra spp.	133	0	600	333	467	333
Scenedesmus spp.	67	67	67	200	67	200
Cryptomonas erosa	2133	2267	3467	2933	2333	2667

*Density, number per liter

Table 2b. July Phytoplankton in the Duluth-Superior Harbor, 1982.

Species	Sites					
	A	B	C	E	H	L
Asterionella formosa	133*	67	133	0	333	133
Cocconeis spp.	467	467	267	200	267	200
Cyclotella meneghiniana	3067	933	1867	933	2733	2133
Melosira distans	3067	1600	1600	267	3267	3733
Melosira granulata	867	1667	1267	1067	1733	2133
Melosira spp.	0	67	0	0	0	0
Navicula spp.	400	600	800	133	333	200
Stephanodiscus spp.	67	600	600	67	133	267
Synedra ulna	333	400	467	200	200	200
Synedra spp.	400	400	600	267	200	67
Scenedesmus spp.	133	200	133	0	267	0
Cryptomonas erosa	1067	4533	4200	8800	1067	2133

*Density, number per liter

Table 2c. August Phytoplankton in the Duluth-Superior Harbor, 1982.

Species	Sites					
	A	B	C	E	H	L
Asterionella formosa	67*	133	67	67	67	200
Cocconeis spp.	67	67	0	0	67	0
Cyclotella meneghiniana	733	200	133	67	267	600
Melosira distans	600	1000	1067	1000	1133	1733
Melosira granulata	2867	2667	2067	2000	2867	4200
Melosira spp.	67	333	333	133	467	400
Navicula spp.	333	333	133	67	533	267
Stephanodiscus spp.	133	67	0	0	0	67
Synedra ulna	0	0	0	0	0	0
Synedra spp.	0	67	67	0	67	133
Scenedesmus spp.	133	67	200	133	200	67
Cryptomonas erosa	3067	6600	8533	10,400	5133	1733

*Density, number per liter.

Table 3. Chlorophyll *a* Concentrations from the Duluth-Superior Harbor, Summer, 1982 (ug/liter).

Site*	June 17	July 22	August 18
A	0.90	3.50	0.70
B	1.10	5.00	0.75
C	1.20	4.00	0.70
E	0.90	4.00	1.10
H	0.75	0.20	1.00
L	0.85	3.00	0.60

*Reference Figure 1.

Concentrations of Chlorophyll a measured from each site are presented by date in Table 3. The usual pattern for north temperate waters is seen in the harbor, as well: Chlorophyll values climb into July and drop quickly as solar radiation and water temperatures diminish. We conclude once more that all sites demonstrate the same essential pattern (p .05, two-way ANOVA) as we did from the species list information (Sokal and Rohlf, 1969). The one interesting departure, site "H" on July 22, shows a value one order of magnitude lower than its companions. This site is the offshore site in the WLSSD Bay. All standards and procedures were double-checked for this sample - the value is correctly reported. This probably indicates the sort of variability that can be expected when sampling near the dredged channels, the deeper waters of which contain less chlorophyll than the uppermost layers. Light attenuation, rapidly in the uppermost layers, must be an extremely important factor influencing phytoplankton life in the Harbor.

The zooplankton of the harbor, judging from these six sites, become dominated by Bosmina coregoni (some specimens bear features of B. longirostris) as summer progresses. Table 4 displays the thirteen taxonomic categories into which zooplankton were enumerated. Table 5 illustrates the volumes of Harbor water filtered per sample at each site during the summer. Triplicate samples were taken each time. At times, Bosmina so dominated the community that they appeared to "swarm". This became more prominent later in mid-summer as the more cool-water species like Daphnia galeata and the Diaptomus spp. declined. From Table 6a, b, and c, the clear dominance of just a few species within the community can be seen. The pattern persisted at each of the sites sampled. Further, the same species were dominant at all six sites at one particular time, though the magnitude of this dominance varied. Only eight species figured importantly in the zooplankton community structure, however, eleven taxa plus a

Table 4. Composite List of Zooplankton from Six Sites in the Duluth-Superior Harbor, Summer, 1982.

Category 1 - Cladocera

Daphnia galeata

Bosmina coregoni

Diaphanosoma leuctenbergianum

Leptodora kindtii

Ceriodaphnia megalops

Alona guttata

Category 2 - Copepoda

Diaptomus spp.

Mesocyclops leuckarti

Paracyclops fimbriatus

Halicyclops spp.

Orthocyclops modestus

Category 3

Immature copepods (nauplii & copepodites)

Harpacticoida

Table 5. Volumes Filtered in Zooplankton Collection (liters) at Six Sites in the Duluth-Superior Harbor during Summer, 1982

	A	B	C	E	H	L
June	73.6	24.5	61.4	30.7	24.5	73.6
July	73.6	24.5	15.3	24.5	36.8	73.6
August	73.6	24.5	30.7	36.8	36.8	85.9

category of immature copepods (nauplii and copepodites) were enumerated along with an occasional errant Harpacticoid copepod-up from the sediments.

The June data (Table 6a) illustrate an interesting phenomenon around station E, the WLSSD effluent. The production of immature copepods is ahead here relative to the rest of our sites. I suspect the warmth of the effluent to be the principal cause. The numbers of immatures are elevated 10 - 15X over those in the two comparison bays in June. This relationship is still somewhat apparent in July, but disappears by August. This could be an indirect effect - the warmth causing accelerated algal growth, algae used as food by the copepods.

In July (Table 6b) the overall community was quite reduced, but densities were highest in the WLSSD Bay. Halicyclops spp. which pervade the bay were most abundant at station E, near WLSSD. This genus is known for its tolerance to brackish-salty conditions (Edmondson, 1959).

Table 6a. June Zooplankton in the Duluth-Superior Harbor, 1982 (no. per liter).

	Sites					
Zooplankton	A	B	C	E	H	L
Daphnia galeata	6.94	8.41	9.66	3.88	9.59	9.43
Bosmina coregoni	31.89	29.02	49.44	77.04	40.61	178.56
Diaphanosoma leuctenbergianum	.34	1.18	2.10	1.56	.37	3.40
Leptodora kindii	.10	.65	.28	.00	.00	.00
Ceriodaphnia megalops	.00	.00	.00	.00	.00	.00
Alona guttata	.00	.00	.00	.00	.00	.00
Diaptomus spp.	3.95	2.29	.44	3.68	1.88	1.89
Mesocyclops leuckarti	.42	.24	.73	20.03	10.16	2.27
Paracyclops fimbriatus	.93	.53	1.14	.33	1.31	2.27
Halicyclops spp.	1.68	2.86	3.93	10.07	.65	4.52
Orthocyclops modestus	.00	.00	.00	.00	.00	.00
Immature copepods	7.82	18.24	24.54	211.50	6.78	71.30
Harpacticoida	.00	.00	.00	.00	.00	.00

Table 6b. July Zooplankton in the Duluth-Superior Harbor, 1982 (no. per liter).

	Sites					
Zooplankton	A	B	C	E	H	L
Daphnia galeata	.26	.53	.78	1.14	.24	.61
Bosmina coregoni	.91	2.00	6.60	17.39	2.26	2.02
Diaphanosoma leucten bergianum	.23	.33	.92	1.47	.11	.07
Leptodora kindtii	.00	.00	.00	.00	.00	.00
Ceriodaphnia megalops	.04	.04	.00	.00	.00	.00
Alona guttata	.01	.04	.07	.00	.03	.00
Diaptomus spp.	.15	.37	.26	1.35	.38	.57
Mesocyclops leuckarti	.03	.08	.72	.61	.16	.20
Paracyclops fimbriatus	.12	.37	.39	2.08	.22	.39
Halicyclops spp.	.92	5.76	2.35	11.43	.73	1.20
Orthocyclops modestus	.00	.00	.00	.00	.05	.10
Immature copepods	5.39	9.63	11.05	54.82	4.65	8.14
Harpacticoida	.03	.00	.00	.00	.00	.01

Table 6c. August Zooplankton in the Duluth-Superior Harbor, 1982 (no. per liter).

Zooplankton	Sites A	B	C	E	H	L
Daphnia galerta	19.35	24.24	13.75	6.36	7.42	3.02
Bosmina coregoni	9.10	29.63	19.71	25.79	17.17	6.29
Diaphanosoma leucten bergianum	9.46	8.20	5.67	3.34	3.89	1.71
Leptodora kindtii	.08	.00	.00	.00	.00	.00
Ceriodaphnia megalops	.30	1.02	.72	.19	.19	.08
Alona guttata	.00	.00	.00	.00	.00	.00
Diaptomus spp.	4.16	3.84	4.36	8.07	5.16	4.37
Mesocyclops leuckarti	1.44	4.82	2.61	6.85	3.45	1.70
Paracyclops fimbriatus	3.70	9.39	4.07	6.85	3.23	1.65
Halicyclops spp.	3.10	9.47	3.84	7.23	4.27	1.65
Orthocyclops modestus	.00	.00	.00	.00	.00	.00
Immature copepods	16.70	37.39	17.10	25.73	18.67	10.98
Harpacticoida	.00	.00	.00	.00	.00	.00

August (Table 6c) showed higher densities overall for the zooplankton in the Harbor. Relatively large gains were made by Diaphanosoma and Ceriodaphnia, which made its first appearance in our samples from four of the six sites. Their densities were greatest in the open water stations and the control bays (sites A, L and B, C). The population increases of these species probably paralleled the development of adequate bacteria, phytoplankton or periphyton food supplies.

The Duluth-Superior Harbor is a complex system for pelagic sampling. Not only is the bathymetry complex, with the extensive shallows plus the deep, dredged ship channels, but the interactive flows of the St. Louis River and seiche currents from Lake Superior make point samples a function of many variables. In the shallows, particularly, the range of seasonal change can be extreme. Within this context, examination of the plankton data from Summer 1982 shows no adverse influence of the effluent from the Western Lake Superior Sanitary District.

Literature Cited

Edmondson, W.T. (ed.). 1959. Fresh-Water Biology, 2nd Ed. Wiley & Sons, New York.

Edmondson, W.T. and G.G. Winberg. 1971. A manual on methods for the assessment of secondary productivity in freshwaters. IBP Handbook No. 17. Blackwell, Oxford.

Fogg, G.E. 1975. Algal cultures and phytoplankton ecology, 2nd ed. University Wisconsin Press, Madison.

McNabb, C.D. 1960. Enumeration of freshwater phytoplankton concentrated on the membrane filter. Limnol. Oceanogr. 5:57-61.

Pennak, R.W. 1978. Fresh-Water Invertebrates of the United States, 2nd Ed. Wiley & Sons, New York.

Sokal, R.R. and F.J. Rohlf. 1969. Biometry. Freeman, San Francisco.

Strickland, J.D.H. and T.R. Parsons. 1972. A practical handbook of seawater analysis. Bull. 167. Fish. Res. Board Canada.

Wetzel, R.G. 1975. Limnology. Saunders Company, Philadelphia.

Summary

Ventilatory Response of Bluegill Sunfish Exposed to Final Treated WLSSD Effluent

by

Robert A. Drummond, Research Aquatic Biologist

U.S. Environmental Protection Agency

Environmental Research Laboratory-Duluth

6201 Congdon Boulevard

Duluth, Minnesota 55804

December 1982

The ventilatory activities (cough and opercular rates) of two bluegills exposed to 100% final-treated effluent (continuous flow-through) were monitored over an extended period of time. A synopsis of this monitoring effort follows.

Two fish were installed on August 18, 1982, and allowed to recover from the effects of transfer for 24-hours. Starting August 19, the fish were monitored continuously for the next 96-hours and all respiratory data was recorded on strip-chart records. At least one major period of stress was noted to occur; at other times the fish appeared normal, i.e., similar to several hundred controls observed at ERL-D in Lake Superior water.

After 96-hours, fish were monitored nearly every day for the next month. New fish were installed on August 27 and on September 10, 1982. During this period, treatment plant operators would turn the strip-chart monitor on for time slots ranging from 2 to 12 hours per day. Occasionally the fish were monitored even longer.

Respiratory data were plotted at half-hour intervals on the basis of relative change from the expected normal. Three categories were designated: some stress evident, moderate stress, and highly stressed. It was apparent from these data plots that the effluent was not of consistent quality from hour-to-hour or day-to-day. At least one period of high stress was correlated to the presence of residual chlorine. Another period of stress appeared to be correlated with changes in influent quality as a result of industrial housekeeping activities. University of Wisconsin personnel conducting on-site exposures observed mortalities among fathead minnows during this same period (circa September 1 - 7). Other peak periods of response were of unknown cause.

All original data plots were turned over to Mr. Duane Long at WLSSD for study and comparison of these events with treatment plant operations.

SITE-SPECIFIC ACUTE AND CHRONIC AQUATIC TOXICITY TESTING--WESTERN LAKE SUPERIOR SANITARY DISTRICT TREATMENT PLANT EFFLUENT STUDIES

By

Daniel J. Call, Larry T. Brooke,
Carol Northcott, and Dean E. Hammermeister

Center for Lake Superior Environmental Studies
University of Wisconsin-Superior

November 1982

U.S. EPA Cooperative Agreement No. CR80923402

SITE-SPECIFIC ACUTE AND CHRONIC AQUATIC TOXICITY TESTING--WESTERN LAKE SUPERIOR SANITARY DISTRICT TREATMENT PLANT EFFLUENT STUDIES

INTRODUCTION

A need exists for the characterization of natural waters regarding their capacities for reducing the toxic effects of discharged wastes to aquatic organisms. An understanding of effects of naturally occurring ligands in reducing toxicities of various wastes would facilitate the issuance of variances for discharge permit limits upon an environmentally sound site-specific basis.

A study was conducted by the University of Wisconsin-Superior, Superior, WI, to determine the toxicity to aquatic organisms of effluent from the Western Lake Superior Sanitary District (WLSSD) treatment facility in Duluth, MN. Exposures were conducted on site and at the University of Wisconsin-Superior campus with organisms native to the area and thought to have a high level of sensitivity to potentially toxic effluent. Water from the St. Louis River upstream from the WLSSD discharge point and University of Wisconsin laboratory water were used as the control water.

Bioassays were conducted using static and flowing conditions with grab and composited samples of two processed waters within the WLSSD treatment plant and seven species of aquatic organisms. Water samples were collected at various times throughout the summer of 1982.

METHODS

Test Water Description

WLSSD treatment plant processed waters and St. Louis River water were employed as test waters. WLSSD water was examined for suspected toxicity while the river water was used as a 'clean' water control for comparison.

Two types of WLSSD treatment plant processed waters were tested - filtered and final effluent. Filtered effluent was water which had been fully treated except for chlorination. This water was called filtered effluent because it is filtered immediately prior to chlorination. Final effluent was filtered effluent that had been chlorinated and subsequently dechlorinated before discharge to the harbor. Filtered effluent was not released to the harbor during this study without chlorination and dechlorination.

St. Louis River water was collected by submerging 5 gal polypropylene carboys at a site located at the end of the City of Superior, WI boat landing pier on the downstream side of the Arrowhead bridge.

Water Chemistry Determinations

Measurements of pH (Method 424), total alkalinity (Method 403), total hardness (Method 309 B) and dissolved oxygen (Method 422 B) were made on exposure water samples according to Standard Methods for the Examination of Water and Wastewater (APHA, 1975). Water analysis was performed once either at the start or during the exposure period for static bioassays. For the flow-through tests, samples for pH, alkalinity, and hardness were taken every day while dissolved oxygen was measured at least every other day. Alkalinity and pH determinations were completed on the same day they were taken or stored at 3 C overnight before the measurements were made. Samples from the WLSSD treatment plant for hardness determination required fivefold dilution prior to analysis. Without dilution,

the hardness endpoint was not clear. Chlorine content and pH of the tested effluents at the time of discharge are available from WLSSD records and not reported in this report.

Results of final effluent exposure water chemistry measurements made during the study period were quite variable. The geometric mean pH was 7.76 and ranged from 6.7 to 8.6. The mean total alkalinity was 214 $mg \cdot L^{-1}$ as $CaCO_3$ with a range from 147 to 362 $mg \cdot L^{-1}$. The mean value for total hardness was 210 $mg \cdot L^{-1}$ as $CaCO_3$, ranging from 121 to 252 $mg \cdot L^{-1}$. The mean and standard deviation of dissolved oxygen concentrations were 6.8 ± 1.0 $mg \cdot L^{-1}$ (n=118).

Results of filtered effluent exposure water chemistry determinations were also highly variable. The geometric mean pH was 7.95 with a range of 6.5 to 8.6 The mean total alkalinity was 193 $mg \cdot L^{-1}$ as $CaCO_3$, ranging from 142 to 278 $mg \cdot L^{-1}$. Mean total hardness was 235 $mg \cdot L^{-1}$ as $CaCO_3$ and ranged from 208 to 267 $mg \cdot L^{-1}$. The mean and standard deviation of dissolved oxygen concentrations were 6.8 ± 0.9 $mg \cdot L^{-1}$ (n=88).

Organisms

Test organisms used during the series of exposures included Daphnia magna, (water flea), Gammarus pseudolimnaeus, Hyalella azteca (amphipods), Pimephales promelas (fathead minnow), Diplectrona sp. (caddis fly), Hexagenia sp. and Stenonema sp. (mayflies). D. magna were cultured at the University of Wisconsin-Superior with 30 mg of yeast and trout chow (4:1 wt:wt) per liter of water. G. pseudolimnaeus were collected from the Eau Claire River upstream of the city of Gordon, WI on 17 March, 1982. On the same date, H. azteca were collected from the St. Croix River immediately below the St. Croix Flowage dam near Gordon, WI. The amphipods were held at 15 C and fed ground, dried, maple leaves prior to exposure. Fathead minnows were reared in the University of Wisconsin-

Superior culture facilities and fed 48 hr old Artemia sp. (brine shrimp) until testing. Diplectrona sp., Hexagenia sp. and Stenonema sp. were all collected on 9 August 1982 from Mission Creek at Fond du Lac, MN, the Brule River at the Wisconsin Ranger Station, Brule, WI and from Interfalls Lake at Pattison Park, WI, respectively.

During all tests observation for mortalities were made at least once daily.

Static Bioassays

Static tests were conducted on grab samples and on one day and seven day composite samples of WLSSD effluent collected at different times throughout the summer. The tests were run at the University at room temperature which ranged from 21-23 C for the exposures.

The 14 June, 1982, effluent was screened for toxicity with five 30 day-old P. promelas, six G. pseudolimnaeus and eleven H. azteca. They were all tested in 1 L beakers containing 900 mL of the grab sample. In addition, five young P. promelas and five D. magna were tested in 250 mL beakers containing 200 mL of grab sample.

Static exposures performed from 23 June through 2 August, 1982 used grab and one or seven day composite samples of WLSSD effluent. Quadruplicate exposures of five P. promelas and five D. magna in 200 mL of 100% effluent were made in 250 mL beakers. For each exposure, quadruplicate control exposures were performed using laboratory water from the University of Wisconsin-Superior.

Grab samples of WLSSD effluent taken on 8, 9, and 10 September, 1982, were used to expose P. promelas. The samples were diluted with St. Louis River water to provide 0, 25, 50, 75, and 100 percent solutions in duplicate. Ten fish total were exposed to each concentration.

Flow-Through System Description

A continuous flow system was designed to expose various types of organisms to the WLSSD treatment plant final effluent and to St. Louis River water. Temperature control and aeration were provided to the test waters. Organisms were exposed to 100% final effluent and 100% St. Louis River water. An identical exposure apparatus was used for each water type. The apparatus consisted of an exposure tank within a larger tank (water bath). Two types of exposure tanks were employed throughout the three month test period: a large tank into which two small compartmental inserts were placed and a smaller exposure tank with no compartments. Each exposure tank was equipped with a stand pipe and drain tube. Metering pumps delivered test waters to the exposure tanks via stainless steel tubing. The point of inflow was always opposite the tank stand pipe. The WLSSD final effluent diverted to a sampling box was the source of treatment plant test water. St. Louis River water that was collected periodically was pumped from a 56 L polypropylene reservoir into the other exposure tank. To facilitate temperature control, a flow-splitting tank distributed cold tap water equally to each of the two water bath tanks. Adequate oxygenation was supplied by a dual outlet air pump. An air stone was placed in each exposure tank in the area of test water inflow.

Flow-Through Bioassays

The first flow-through exposures were conducted with *Diplectrona* sp., *Hexagenia* sp., *P. promelas*, and *Stenonema* sp. Five each of *Diplectrona* sp. and *Hexagenia* sp., and ten each of *P. promelas* and *Stenonema* sp., were exposed in duplicate. To separate the organisms and expose them in duplicate, two 3 compartment inserts and two stainless steel mesh cages were used within a large exposure tank that measured 34.5 x 20.5 x 10.5 cm. The inserts measured

15.0 x 15.4 x 13.8 cm and had two ends covered with 505 μm Nytex® mesh to allow water exchange. The cages were 9.4 cm long by 4.0 cm in diameter and closed with a neoprene stopper. Ten Stenonema sp. were loaded in each of the cages and positioned in the center of insert compartments. The other organisms were exposed separately in insert compartments. The tank volume exchange rate with final effluent was 5.8 volumes·day^{-1}.

In the second flow-through exposure, twenty fathead minnows were placed into a tank 9.8 x 23 x 11.8 cm containing 2.65 L of water. Flow was increased to provide 20 tank volume exchanges·day^{-1}.

In both exposures a duplicate system was operating using St. Louis River water, collected daily, as a reference. All chambers were covered with a glass plate to prevent contamination and evaporation.

RESULTS

Bioassays of WLSSD effluents (prior to chlorination and immediately after dechlorination) were conducted with waters sampled 14 June through 10 September 1982. Both static and flow-through assays were conducted, with the static tests performed at the UW-Superior testing facility and the flow-through testing done at the WLSSD treatment facility.

Static Bioassays

Twenty-three tests were run with WLSSD effluent and St. Louis River reference water. Four species of aquatic organisms (P. promelas, G. pseudo-limnaeus, H. azteca, and D. magna) were included in the tests. Water samples were collected on thirteen occasions from three sites (St. Louis River, WLSSD effluent after final filtering prior to chlorination, and final processed water after chlorination and dechlorination). Some deaths occurred in St. Louis River

reference water in 26.1% of the tests. Similar numbers of deaths in reference and processed waters precluded the use of bioassay data with Daphnia for the composited water samples collected on July 12 and 19 and with P. promelas for water samples collected on July 13 and September 9. Filtered effluent from WLSSD had increased toxicity when compared to St. Louis River water in 46.2% of the remaining tests (Table 1) and the final WLSSD effluent showed increased toxicity when compared to St. Louis River water in 38.9% of the remaining tests. However, mortalities of 5-10% represented the deaths of only 1-2 organisms.

The greatest differences in mortalities of organisms in reference and processed waters were with P. promelas and grab samples of the final effluent collected on 29 July, 8 September, and 10 September. On these three dates (23.1% of sampling dates), mortalities ranged from 33 to 100% in the undiluted final effluent. A portion of the samples collected on 29 July and 10 September were held seven days with aeration and retested with P. promelas. Toxicity was reduced from the initial tests. Mortalities decreased from 40 to 5% for the 29 July grab sample and from 100 to 0% for the 10 September grab sample (Table 1).

Toxicity of the 10 September final effluent was estimated by diluting the effluent with St. Louis River water and exposing P. promelas for 96 hr. The dilutions were 25, 50, and 75% of the processed water. A Spearman-Karber (trimmed) estimate was made of the median lethal concentration (LC_{50}) for this water sample (Hamilton, et al. 1977). The 96 hr LC_{50} was 55.4% of pure processed water.

Flow-Through Bioassays

Initially, four species of aquatic organisms (P. promelas, Hexagenia sp., Stenonema sp., and Diplectrona sp.) were exposed to St. Louis River water and WLSSD final effluent for 96 hr starting on August 16. The St. Louis River

TABLE 1. Effects upon Survival of Several Species of Aquatic Organisms Exposed to St. Louis River Water (Reference) and Two Processed Waters of the Western Lake Superior Sanitary District (WLSSD) for 96 hr. Processed Waters were Sampled at the Stated Times by Instantaneous Grabs or by Compositing with a Pump for 1 or 7 Days. Reference Waters were all Grab Samples. Exposure Water Temperatures were 21-23 C.

Processed Water Collection					Percent Mortality		
Date	Time	Type	Exposed Species	Age	Reference	Filter[a]	Final[a]
6/14	1430	Grab	Pimephales promelas	3 day	0	0	0
				30 day	0	0	0
			Gammarus pseudolimnaeus	adult	0	0	0
			Hyalella azteca	adult	0	9.1	0
			Daphnia magna	adult	0	0	0
6/23	1455	Grab	Pimephales promelas	9 day	0	10	0
			Daphnia magna	adult	0	20	5
6/29	0838	Grab	Pimephales promelas	3 day	0	10	0
6/30	1115	Grab	Pimephales promelas	5 day	0	8.3	9.8
7/12		7-day Composite	Pimephales promelas	9 day	0	0	N.T.[b]
			Daphnia magna	adult	11.8	5.0	N.T.
7/13		1 day Composite	Pimephales promelas	10 day	5	4.8	5
7/19		1 day Composite	Pimephales promelas	11 day	0	0	0
			Daphnia magna	adult	11.8	20	10
7/19		7 day Composite	Daphnia magna[c]	adult	0	5	0
7/29	1430	Grab	Pimephales promelas	5 day	10	N.T.	40
7/29[d]	1430	Grab	Pimephales promelas[e]	13 day	0	N.T.	5
			Pimephales promelas	13 day	0	N.T.	5
8/2	a.m.	Grab[f]	Pimephales promelas[e]	5 day	0	0	5
9/8	p.m.	Grab	Pimephales promelas[g]	0-5 day	10	N.T.	33
9/9	a.m.	Grab	Pimephales promelas[g]	1-6 day	10	N.T.	9.1
9/10	a.m.	Grab	Pimephales promelas[g]	2-7 day	0	N.T.	100
9/10[h]	a.m.	Grab	Pimephales promelas[g]	8-13 day	0	N.T.	0

a/ Filter is processed water immediately prior to chlorination. Final is the chlorinated and dechlorinated processed water as it leaves the treatment facility. Filter water was aerated during testing, final water was aerated only at stated times (see footnotes e & g).
b/ N.T. = not tested.
c/ 48 h exposure.
d/ Water collected on 7/29 was held and retested on 8/6.
e/ Continuous aeration during exposure to final processed water.
f/ Water collected on 8/2 was aerated and held for testing until 8/7.
g/ Daily 15 minute aeration during exposure.
h/ Water collected on 9/10 held at room temperature and retested on 9/17.

reference water consisted of daily grab samples collected upstream at the Arrowhead bridge and WLSSD final effluent pumped continuously from the treatment plant discharge line. No significant ($p \leq 0.05$) differences were observed in mortalities between the two tested waters. However, high mortalities in the controls occurred with the exception of the Stenonema bioassay, where no control organisms died. Ten percent mortality occurred in the final effluent test water with Stenonema.

An extended acute flow-through exposure of P. promelas to WLSSD final effluent was then conducted between 1 September and 8 September. The test was designed to proceed for 30 days to observe fish for possible growth differences. However, at 192 hr the test was terminated due to mortality of all organisms in the final effluent test water (Table 2). The reference or control water was St. Louis River water in which 95% of the fish survived the 192 hr exposure.

TABLE 2. On-Site Flow-Through Extended Acute Bioassay of Western Lake Superior Sanitary District (WLSSD) Final Process Water with Pimephales promelas[a/]

Date	Duration	Percent Mortality	
		St. Louis River	Final Effluent
9/1	24 h	0	0
9/2	48 h	0	0
9/3-6	72-144 h	5	<20[b/]
9/7	168 h	5	<50[b/]
9/8	192 h	5	100

a/ Fathead minnows were 15 days old at the start of the extended acute exposure.

b/ Effluent was highly colored and percentages are approximations based on observations of netted fish on 9/7 and 9/8.

DISCUSSION

The processed water discharged from the WLSSD treatment facility is not continuously toxic to aquatic organisms on an acute basis. However, significant toxicity does periodically occur. In 23.1% of the samples collected from 14 June to 10 September, 1982, mortalities to fathead minnows in the undiluted final effluent ranged from 33 to 100%.

The grab sample of final effluent collected on 10 September resulted in 100% mortality. When this effluent was diluted with St. Louis River water, the resultant LC_{50} to fathead minnows was 55.4% of the pure processed water. From this it would appear that the mixture of WLSSD final effluent and harbor water would be acutely toxic at times to organisms in the immediate vicinity of the diffuser pipes where the effluent is discharged. Dependent upon the total volume of St. Louis River water for dilution of the WLSSD effluent, toxicity would be diminished as distance from the diffuser pipes increased. The dilution factor can be determined from other studies.

The observation that acute toxicity of the final processed water from WLSSD was greatly reduced upon holding with aeration for a period of seven days indicated that the chemical agents responsible for the toxic effects were volatile or chemically unstable in the water. One possible cause for the observed periodic toxicity that was examined was the concentration of total residual chlorine in the final effluent. Records of the chlorine feed rate and chlorine concentrations in the mixer and final effluent were obtained from WLSSD (Figure 1). Elevated concentrations of chlorine in the final effluent were recorded on 6 September and 9-10 September. Grab samples of final effluent collected on 8 and 10 September resulted in 33 and 100% mortality, respectively, to fathead minnows in static bioassay. The 96 hr LC_{50} for total residual chlorine with fathead minnows was

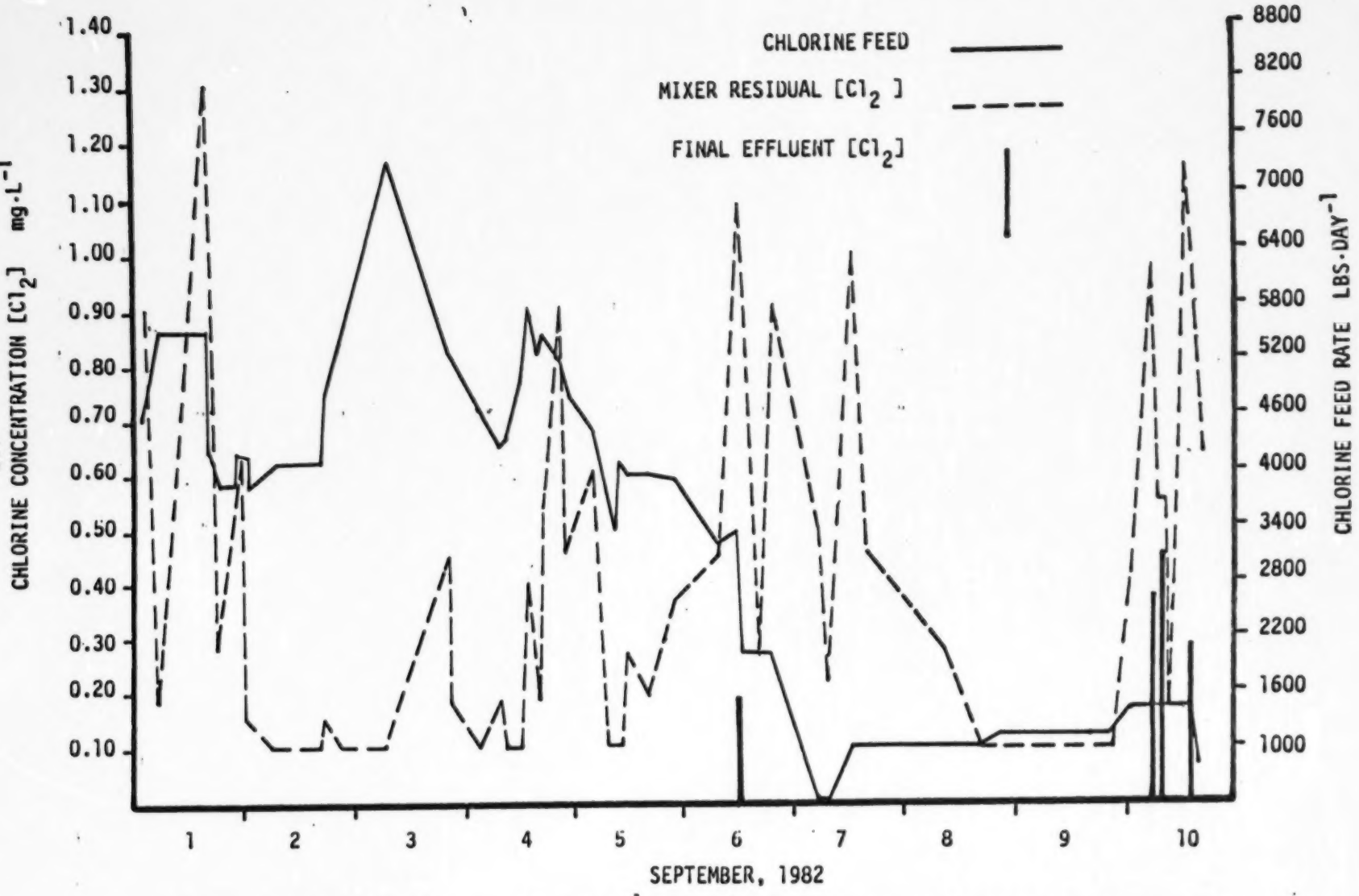


Figure 1. Chlorine feed rate ($lbs \cdot day^{-1}$) and concentrations of chlorine in the mixer and final effluent ($mg \cdot L^{-1}$) at the WLSSD wastewater treatment facility from September 1 to September 10, 1982.

reported as 130 and 86 $\mu g \cdot L^{-1}$ in two separate tests (Arthur et al., 1975). The 24 hr LC_{50} for fathead minnows was 145 and 140 $\mu g \cdot L^{-1}$ as determined by the same authors.

On 6 September, the final effluent chlorine concentration reached a recorded high value of 180 $\mu g \cdot L^{-1}$ and on 9-10 September the concentration for the three recorded spikes ranged from 270 to 450 $\mu g \cdot L^{-1}$. The toxicity of the final effluent grab sample collected on 10 September may have been caused by elevated concentrations of chlorine on that date. However, possible causes for the mortalities in the static bioassays conducted with grab samples collected on 29 July and 8 September are not known.

In the extended acute flow-through exposure with young fathead minnows that started on 1 September, mortalities began occurring between 3 and 6 September, with complete mortality occurring by 8 September. These mortalities may have resulted from the elevated chlorine concentration on 6 September.

WLSSD personnel indicated that excess carbon dioxide (CO_2) may occasionally be present in sufficient concentrations to cause mortality of fathead minnows. Evidence of high CO_2 content of the final effluent does exist, although no CO_2 measurements were made in this study.

The pH of some grab samples increased with time. Samples taken on 8, 9 and 10 September 1982 had an initial pH of 6.95, 6.81 and 6.61, respectively (WLSSD records). They exhibited a gradual increase of pH to 8.12, 8.55 and 8.45, respectively, when held 1 day for bioassay testing. Five water samples taken during the period, 1 September to 5 September 1982, had a mean pH of 7.13 and ranged from 7.05 to 7.21 when measured within 6 hr after sampling. They exhibited an increase of 0.45 to 0.60 pH units according to plant records of pH for final effluent discharged during this period. It is not known whether these five

samples would have increased to a pH greater than 8.1 as did samples taken during the later sampling period.

During the second flow-through bioassay the total alkalinity of bioassay water was frequently much greater than hardness. For final effluent grab samples taken on 8, 9, and 10 September and analyzed at the end of acute bioassay exposures, the total alkalinity was 317, 362 and 236 $mg \cdot L^{-1}$ as $CaCO_3$, respectively. Corresponding hardness values were 152, 141, and 121 $mg \cdot L^{-1}$ as $CaCO_3$, respectively. The differences between alkalinity and hardness are greater than that of samples taken earlier in the study. Alkalinity and hardness values for the time period 1 September to 5 September 1982 had a mean of 218 and 174, respectively, with a range of values from 210 to 235 and 165 to 187, respectively. The interaction of high pH influent from the Potlatch Corporation with other influent and process waters already within the plant may result in a temporary buffering of the final effluent.

Discharge water from the Potlatch Corporation passes through the Cloquet pumping station and travels to the WLSSD treatment plant where it mixes with other plant influent waters. Highly alkaline discharge water from the Potlatch Corporation reached the Cloquet station approximately at 9:00 a.m., 6 September and continued until termination of our testing on 10 September, 1982. The mean and range of pH values for Cloquet station effluent was 10.36, and 8.77 to 11.32, respectively. Approximately 21 hrs later, the beginning of the alkaline water arrived at the treatment plant influent point, as indicated by a pH increase from 7.48 to 8.14 in 1 hr. For the period 6 September to 9 September, 1982, final effluent mean pH was 6.82 and the range of pH was 6.45 to 7.17. In comparison, final effluent mean pH was 6.59 and ranged from 6.45 to 6.81 during the period 1 September to 5 September, 1982. Alkaline influent was not present then.

Carbon dioxide is readily dissolved into an alkaline solution and the concentration of HCO^-_3 and $CO_3^=$ are allowed to increase, subsequently increasing carbonate alkalinity. This is the condition that existed in the Potlatch effluent from 6 to 10 September. Apparently, in-plant precipitation, complexation, and dilution by other influents are sufficient to maintain a final effluent pH near neutrality with elevated alkalinity during the time highly alkaline Potlatch effluent is present.

During the secondary treatment process microbial respiration produces some CO_2 but an excess of free CO_2 may already have been present in the influent. This would tend to preserve the high alkalinity of alkaline influent; that is, it would allow relatively large amounts of CO_2 to remain in solution as HCO^-_3 as $CO_3^=$. When the process waters pass from the region of high free CO_2 concentration to a region of lower concentration, CO_2 is evolved according to the following reactions.

$$CO_3^{(=)} + H_2O \rightleftharpoons HCO_3^{(-)} + OH^{(-)}$$

$$HCO_3^{(-)} + H_2O \rightleftharpoons H_2CO_3 + OH^{(-)}$$

$$H_2CO_3 \rightleftharpoons H_2O + CO_2$$

When CO_2 is evolved, hydroxyl ion (OH^-) is produced, raising pH of final effluent. These reactions are probably responsible for the pH increase observed for the grab samples described earlier.

This mechanism, although simplistic, may explain a probable cause for the gradual pH increase, marked difference between alkalinity and hardness of final effluent when alkaline influent was present and possibly, test organism mortalities. All of the factors which influence CO_2 concentrations are not

accounted for. High free CO_2 concentrations may have occurred at other times during the study and may be associated with conditions other than alkaline influent.

REFERENCES

American Public Health Association. 1975. Standard Methods for the Examination of Water and Wastewater (14th ed.). American Public Health Association, Washington, D.C.

Arthur, J.W., R.W. Andrew, V.R. Mattson, D.T. Olson, G.E. Glass, B.J. Halligan, and C.T. Walbridge. 1975. Comparative toxicity of sewage-effluent distribution to freshwater aquatic life. U.S. Environmental Protection Agency, Duluth, MN. Ecological Research Series EPA-600/3-75-012.

Hamilton, M.A., R.C. Russo, and R.V. Thurston. 1977. Trimmed Spearman-Karber Method for estimating median lethal concentrations in toxicity bioassays. Environ. Sci. Technol. 11:714-719. Correction 12:417(1978).

Summary

Characterization of the Organic Nature of the Western Lake Superior Sanitary District Effluent Summer, 1982 (Subtask 1)

Prepared by

Ronald Caple

Department of Chemistry

Lake Superior Basin Studies Center

214 Research Laboratory Building

University of Minnesota-Duluth

Duluth, Minnesota 55812

February, 1983

The University of Minnesota is committed to the policy that all persons shall have equal access to its programs, facilities and employment without regard to race, creed, color, sex, national origin or handicap.

The objective of this portion of the project was to identify as many of the organic components in the Western Lake Superior Sanitary District (WLSSD) effluent as possible. To make this complex task more meaningful, a similar analysis was undertaken of the WLSSD affluent, as well as the effluent of the Potlatch paper mill operations in Cloquet, Minnesota. The latter is suspected to be the largest single contributor of industrial type organics to the WLSSD operation.

The qualitative analyses of the above three sites was the result of coordinated sampling that gave a composite sample at each of those sites corresponding as closely as possible to the same flow through sample. The isolation and concentration of the organics in these composite samples was done in threes to reflect the "acidic", "neutral", and "basic" functionalities in the components. The chemical analyses were done by mass spectroscopy. The mass of data obtained are presently being incorporated into a three x three matrix (3 analyses at 3 sample sites) based on functionality.

A two-pronged approach to the analyses of chlorophenols was developed in the event this would be useful for future monitoring purposes. The procedures were complementary in that one was a gas chromatography with electron capture detection (GC-ECD) approach aimed at sensitivity, and the second procedure used liquid chromatography (HPLC) with a variable wavelength detector that, with wavelength ratioing as a tool for identification, would aid in the identification of chlorophenols in complex mixtures. The GC-ECD method involved a prior derivatization with acetic anhydride which led to enhanced extraction efficiencies, whereas the HPLC analyses, while not as sensitive without prior concentration, did not require derivatization.

A procedure has been optimized for the quantitative analysis of trace phenolic components in environmental samples. Basic solutions that contain the phenolic compounds as their phenoxide salts are acetylated with acetic anhydride. The resulting acetate derivatives of the phenols are readily extractable from an aqueous solution and are easier to handle by common GC techniques.

A detailed report containing the methods used in effluent characterizations and raw data, and chlorophenol analyses procedures are available on request.